

Wettability Literature Survey— Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability

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Summary. Wettability is a major factor controlling the location, flow, and distribution of fluids in a reservoir. The wettability of a core will affect almost all types of core analyses, including capillary pressure, relative permeability, waterflood behavior, electrical properties, and simulated tertiary recovery. The most accurate results are obtained when native- or restored-state cores are run with native crude oil and brine at reservoir temperature and pressure. Such conditions provide cores that have the same wettability as the reservoir.

The wettability of originally water-wet reservoir rock can be altered by the adsorption of polar compounds and/or the deposition of organic material that was originally in the crude oil. The degree of alteration is determined by the interaction of the oil constituents, the mineral surface, and the brine chemistry. The procedures for obtaining native-state, cleaned, and restored-state cores are discussed, as well as the effects of coring, preservation, and experimental conditions on wettability. Also reviewed are methods for artificially controlling the wettability during laboratory experiments.

Introduction

This paper is the first of a series of literature surveys covering the effects of wettability on core analysis.¹⁻³ Changes in wettability have been shown to affect capillary pressure, relative permeability, waterflood behavior, dispersion of tracers, simulated tertiary recovery, irreducible water saturation (IWS), residual oil saturation (ROS), and electrical properties.⁴⁻²⁶ For core analysis to predict the behavior of a reservoir accurately, the wettability of a core must be the same as the wettability of the undisturbed reservoir rock. A serious problem occurs because many aspects of core handling can drastically affect wettability.

Water-Wet, Oil-Wet, and Neutrally Wet. Wettability is defined as "the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids."⁷ In a rock/oil/brine system, it is a measure of the preference that the rock has for either the oil or water. When the rock is water-wet, there is a tendency for water to occupy the small pores and to contact the majority of the rock surface. Similarly, in an oil-wet system, the rock is preferentially in contact with the oil; the location of the two fluids is reversed from the water-wet case, and oil will occupy the small pores and contact the majority of the rock surface. It is important to note, however, that the term wettability is used for the wetting preference of the rock and does not necessarily refer to the fluid that is in contact with the rock at any given time.

For example, consider a clean sandstone core that is saturated with a refined oil. Even though the rock surface is coated with oil, the sandstone core is still preferentially water-wet. This wetting preference can be

demonstrated by allowing water to imbibe into the core. The water will displace the oil from the rock surface, indicating that the rock surface "prefers" to be in contact with water rather than oil. Similarly, a core saturated with water is oil-wet if oil will imbibe into the core and displace water from the rock surface. Depending on the specific interactions of rock, oil, and brine, the wettability of a system can range from strongly water-wet to strongly oil-wet. When the rock has no strong preference for either oil or water, the system is said to be of neutral (or intermediate) wettability. Besides strong and neutral wettability, a third type is fractional wettability, where different areas of the core have different wetting preferences.²⁷

The wettability of the rock/fluid system is important because it is a major factor controlling the location, flow, and distribution of fluids in a reservoir. In general, one of the fluids in a porous medium of uniform wettability that contains at least two immiscible fluids will be the wetting fluid. When the system is in equilibrium, the wetting fluid will completely occupy the smallest pores and be in contact with a majority of the rock surface (assuming, of course, that the saturation of the wetting fluid is sufficiently high). The nonwetting fluid will occupy the centers of the larger pores and form globules that extend over several pores.

In the remainder of this survey, the terms wetting and nonwetting fluid will be used in addition to water-wet and oil-wet. This will help us to draw conclusions about a system with the opposite wettability. The behavior of oil in a water-wet system is very similar to the behavior of water in an oil-wet one. For example, it is generally assumed that for a system with a strong wetting preference, the wetting-phase relative permeability is only a function of

TABLE 1—DISTRIBUTION OF RESERVOIR WETTABILITIES BASED ON CONTACT ANGLE³⁴

	Contact Angle (degrees)	Silicate Reservoirs	Carbonate Reservoirs	Total Reservoirs
Water-wet	0 to 75	13	2	15
Intermediate wet	75 to 105	2	1	3
Oil-wet	105 to 180	15	22	37
Total		30	25	55

its own saturation—i.e., it shows no hysteresis.^{7,12,28} Owens and Archer²⁸ measured the gas/oil drainage permeability, where the oil was the strongly wetting fluid, and compared it with the water/oil imbibition relative permeability, where the water was the strongly wetting fluid. The water-imbibition relative permeability (strongly water-wet system) was a continuation of the oil-drainage relative permeability (strongly oil-wet system), demonstrating the analogy between systems of opposite wettabilities.

Historically, all petroleum reservoirs were believed to be strongly water-wet. This was based on two major facts. First, almost all clean sedimentary rocks are strongly water-wet. Second, sandstone reservoirs were deposited in aqueous environments into which oil later migrated. It was assumed that the connate water would prevent the oil from touching the rock surfaces. In 1934, Nutting²⁹ realized that some producing reservoirs were, in fact, actually strongly oil-wet. He found that the quartz surfaces of the Tensleep sandstone in Wyoming had adsorbed heavy hydrocarbons in layers about 0.7 μm thick (about 1,000 molecules) so firmly that they could not be removed by gasoline or various solvents. When the hydrocarbon film was removed by firing the core, the film could be restored by soaking the cores in crude oil overnight.

Examples of other reservoirs that are generally recognized as strongly oil-wet are the Bradford sands of the Bradford pool, Pennsylvania,³⁰⁻³² and the Ordovician sands of the Oklahoma City field.³³ More recently, Treiber *et al.*³⁴ used the water advancing contact angle to examine the wettability of 55 oil reservoirs. In this procedure, deoxygenated synthetic formation brine and dead anaerobic crudes were tested on quartz and calcite crystals at reservoir temperature. Contact angles (measured through the water) from 0 to 75° [0 to 1.3 rad] were deemed water-wet; from 75 to 105° [1.3 to 1.83 rad], intermediate wet; and from 105 to 180° [1.83 to 3.14 rad], oil-wet. As summarized in Table 1, 37 of the reservoirs tested were classified as oil-wet, 3 were of intermediate wettability, and 15 were water-wet. Most of the oil-wet reservoirs were mildly oil-wet, with a contact angle between 120 and 140° [2.1 and 2.4 rad]. Of the carbonate reservoirs included, 8% were water-wet, 8% were intermediate, and 84% were oil-wet. Most of the carbonate reservoirs were from the west Texas area, however, so there is a geographical bias in the data.

Treiber *et al.* cautioned that these findings could not be considered representative of a truly random sampling of petroleum reservoirs. The samples were biased because (1) all were operations for the same company, (2) most were being considered for some type of flooding, and (3) some of the reservoirs had demonstrated unusual behavior. A fourth consideration is how much the use of degassed fluids rather than the real formation fluids af-

fected the wettability behavior in the contact-angle tests. As discussed later, this probably causes an overestimation of the oil-wetness. Therefore, the large percentage of reservoirs found to be oil-wet is less significant than the general indications that not all reservoirs are water-wet and that the reservoir wettability varies widely.

Contact-angle measurements made by Chilingar and Yen³⁵ suggest that most carbonate reservoirs range from neutrally to oil-wet. They measured the wettability of 161 limestone, dolomitic limestone, calcitic dolomite, and dolomite cores. The cores tested included (1) 90 cores from Asmari limestones and dolomites from the Middle East; (2) 15 dolomite cores from west Texas; (3) 3 cores of Madison limestone from Wyoming; (4) 4 carbonate cores from Mexican oil fields; (5) 4 carbonate cores from the Rengui oil field in the People's Republic of China; (6) 16 carbonate cores from Alberta; (7) 19 chalk cores from the North Sea; (8) 5 samples from India; and (9) 5 samples from Soviet oil fields in the Urals-Volga region. Table 2 shows the distribution of wettabilities with 80% of the reservoirs either oil-wet or strongly oil-wet. Some of the strongly oil-wet reservoirs were oil-wet because of a bitumen coating. Note that the range of contact angles considered to be neutrally wet is smaller than the range given in Table 1. This demonstrates the variation from paper to paper of the cutoff angles between the different wetting states.

As discussed in more detail later, reservoir rock can change from its original, strongly water-wet condition by adsorption of polar compounds and/or the deposition of organic matter originally in the crude oil.^{7,36-42} Some crude oils make a rock oil-wet by depositing a thick organic film on the mineral surfaces. Other crude oils contain polar compounds that can be adsorbed to make the rock more oil-wet. Some of these compounds are sufficiently water soluble to pass through the aqueous phase to the rock.

Fractional Wettability. The realization that rock wettability can be altered by adsorbable crude oil components led to the idea that heterogeneous forms of wettability exist in reservoir rock. Generally, the internal surface of reservoir rock is composed of many minerals with different surface chemistry and adsorption properties, which may lead to variations in wettability. Fractional wettability—also called heterogeneous, spotted, or Dalmation wettability—was proposed by Brown and Fatt²⁷ and others.⁴³⁻⁴⁶ In fractional wettability, crude oil components are strongly adsorbed in certain areas of the rock, so a portion of the rock is strongly oil-wet, while the rest is strongly water-wet. Note that this is conceptually different from intermediate wettability, which assumes that all portions of the rock surface have a slight but equal preference to being wetted by water or oil.

Mixed Wettability. Salathiel⁴⁷ introduced the term mixed wettability for a special type of fractional wettability in which the oil-wet surfaces form continuous paths through the larger pores.⁴⁸⁻⁵⁰ The smaller pores remain water-wet and contain no oil. The fact that all of the oil in a mixed-wettability core is located in the larger oil-wet pores causes a small but finite oil permeability to exist down to very low oil saturations. This in turn permits the drainage of oil during a waterflood to continue until very low oil saturations are reached. Note that the main distinction between mixed and fractional wettability is that the latter implies neither specific locations for the oil-wet surfaces nor continuous oil-wet paths.

Salathiel visualizes the generation of mixed wettability in the following manner. When oil initially invaded an originally water-wet reservoir, it displaced water from the larger pores, while the smaller pores remained water-filled because of capillary forces. A mixed-wettability condition occurred if the oil deposited a layer of oil-wet organic material only on those rock surfaces that were in direct contact with the oil but not on the brine-covered surfaces. Oil-wet deposits would not be formed in the small water-filled pores, allowing them to remain water-wet. The question that Salathiel did not address was how the oil first came into direct contact with the rock. As the oil moves into the larger pores, a thin layer of interstitial water remains on the pore walls, preventing the oil from contacting the rock. Under certain conditions, however, the water film separating the crude and the mineral surface can rupture. Hall *et al.*⁵¹ and Melrose⁵² recently developed a theoretical model for the stability of these thin water films that shows that the water films become thinner and thinner as more oil enters the rock. The water film is stabilized by electrostatic forces arising from the electrical double layers at the oil/water and water/rock interfaces.⁵¹⁻⁵⁴ As the water film thickness is further reduced, a critical thickness is reached where the water films in the larger pores become unstable. The films rupture and are displaced, allowing oil to contact the rock.

Native-State, Cleaned, and Restored-State Cores.

Cores in three different states of preservation are used in core analysis: native state, cleaned, and restored state. The best results for multiphase-type flow analyses are obtained with native-state cores, where alterations to the wettability of the undisturbed reservoir rock are minimized. In this set of papers, the term "native-state" is used for any core that was obtained and stored by methods that preserve the wettability of the reservoir. No distinction is made between cores taken with oil- or water-based fluids, as long as the native wettability is maintained. Be aware, however, that some papers distinguish on the basis of drilling fluid (e.g., see Treiber *et al.*³⁴). In these papers, "native-state" refers *only* to cores taken with a suitable oil-filtrate-type drilling mud, which maintains the original connate water saturation. "Fresh-state" refers to a core with unaltered wettability that was taken with a water-base drilling mud that contains no compounds that can alter core wettability. Here, the term native-state is used for both cases.

The second type of core is the cleaned core, where an attempt is made to remove all the fluids and adsorbed organic material by flowing solvents through the cores. Cleaned cores are usually strongly water-wet and should

TABLE 2—DISTRIBUTION OF CARBONATE RESERVOIR WETTABILITIES³⁵

	Contact Angle (degrees)	Percent of Reservoirs
Water-wet	0 to 80	8
Intermediate wet	80 to 100	12
Oil-wet	100 to 160	65
Strongly oil-wet	160 to 180	15

be used only for such measurements as porosity and air permeability where the wettability will not affect the results.

The third type of core is the restored-state core, in which the native wettability is restored by a three-step process. The core is cleaned and then saturated with brine, followed by crude oil. Finally, the core is aged at reservoir temperature for about 1,000 hours. The methods used to obtain the three different types of cores will be discussed in more detail later.

Factors Affecting the Original Reservoir Wettability

The original strong water-wetness of most reservoir minerals can be altered by the adsorption of polar compounds and/or the deposition of organic matter that was originally in the crude oil.^{7,20,31,32,36-41,55-63} The surface-active agents in the oil are generally believed to be polar compounds that contain oxygen, nitrogen, and/or sulfur.^{36,37,40,41,55,56,64-68} These compounds contain both a polar and a hydrocarbon end. The polar end adsorbs on the rock surface, exposing the hydrocarbon end and making the surface more oil-wet. Experiments have shown that some of these natural surfactants are sufficiently soluble in water to adsorb onto the rock surface after passing through a thin layer of water.^{42,60,69-71}

In addition to the oil composition, the degree to which the wettability is altered by these surfactants is also determined by the pressure, temperature, mineral surface, and brine chemistry, including ionic composition and pH. The effects of pressure and temperature will be discussed later in the section on experimental conditions. The importance of the mineral surface is shown by the contact-angle measurements discussed earlier,^{34,35} in which a large majority of the carbonate reservoirs tested were oil-wet, while many of the sandstone reservoirs were water-wet. Several researchers have found that some polar compounds affect the wettability of sandstone and carbonate surfaces in different ways.^{37,40-42,66,72-76} The chemistry of the brine can also alter the wettability. Multivalent cations sometimes enhance the adsorption of surfactants on the mineral surface.^{34,77-83} The brine pH is also important in determination of the wettability and other interfacial properties of the crude/brine/rock system.^{6,26,84} In alkaline flooding, for example, alkaline chemicals can react with some crudes to produce surfactants that alter wettability.^{6,26}

Surface-Active Compounds in Crude Oil. While the surface-active components of crude are found in a wide range of petroleum fractions,⁴¹ they are more prevalent in the heavier fractions of crude, such as resins and

asphaltenes. These surfactants are believed to be polar compounds that contain oxygen, nitrogen, and/or sulfur. The oxygen compounds, which are usually acidic, include the phenols and a large number of different carboxylic acids.^{67,85,86} Seifert and Howells⁸⁵ showed that the carboxylic acids are interfacially active at alkaline pH. The sulfur compounds include the sulfides and thiophenes, with smaller amounts of other compounds, such as mercaptans and polysulfides.^{87,88} The nitrogen compounds are generally either basic or neutral and include carbazoles, amides, pyridenes, quinolines, and porphyrins.^{40,87-90} The porphyrins can form interfacially active metal/porphyrin complexes with a number of different metals, including nickel, vanadium, iron, copper, zinc, titanium, calcium, and magnesium.⁹¹⁻⁹⁵

Because the surfactants in crude oil are composed of a large number of very complex chemicals that represent only a small fraction of the crude, identifying which compounds are important in altering the wettability has not been possible.^{40,66} In addition, attempts to correlate bulk crude properties with the ability of the crude to alter wettability have been unsuccessful. McGhee *et al.*⁶² saturated Berea cores with brine, oilflooded them to IWS with different crudes, then incubated them at 140°F [60°C] for 1,000 hours to allow the wettability to reach equilibrium. The U.S. Bureau of Mines (USBM) wettability index was then measured and compared with bulk properties of the crude. They found no correlation between the USBM index and interfacial tension (IFT), organic acid content, percent nitrogen, or percent sulfur of the crude. Cuiec⁹⁶ measured the Amott wettability index of restored-state cores and found no correlation between wettability and amounts of acids, bases, aromatics, resins, nitrogen, or sulfur. In all cases, when the restored-state cores were water-wet, the crudes had low asphaltene and sulfur contents. However, other low-asphaltene and low-sulfur crudes rendered cores neutrally or oil-wet.

Experiments that determined the general nature of the surfactants and the crude oil fractions in which they are concentrated without attempting to determine exactly which compounds cause wettability alteration have been more successful. Johansen and Dunning^{97,98} found that asphaltenes were responsible for changing some crude-oil/water/glass systems from water-wet to oil-wet. The system was oil-wet when the crude was used but water-wet when the deasphalted crude was used. The addition of a very small amount (0.25%) of the whole crude to the deasphalted crude restored the oil-wettingness of the system. Donaldson and Crocker⁵⁵ and Donaldson⁵⁶ measured wettability alteration caused by the polar compounds extracted from several different mineral oils. First, the wettability of a series of uncontaminated Berea plugs was measured with brine and a refined mineral oil. The average USBM wettability index was 0.81, or strongly water-wet. After cleaning, the USBM wettability index of the plugs was measured with brine and a 5% mixture of the extracted polar organic compounds in the refined mineral oil. The plugs were significantly less water-wet, with USBM wettability indices ranging from 0.45 (water-wet) to -0.09 (neutrally wet), demonstrating that polar compounds in crude can alter the wettability. Note that there was apparently no aging time with the polar compounds in the plugs, so equilibrium wettabilities may be more strongly oil-wet.

Several researchers^{57,58} analyzed wettability-altering compounds extracted from cores. Jennings⁵⁸ removed a portion of the wettability-altering compounds by extracting a non-water-wet core with toluene, followed by a chloroform/methanol mixture. An imbibition test showed that some of the wettability-altering compounds had been removed during the second extraction because the core was more water-wet. The material removed during the second extraction contained porphyrins and high-molecular-weight paraffinic and aromatic compounds.

Denekas *et al.*⁴¹ used a distillation process to separate crude oils into fractions of different molecular weight. A clean, dry core was saturated with the crude oil fraction to be tested, then aged for 24 hours. An imbibition test based on the relative rate of imbibition was used to determine the wettability alteration.^{1,41} The original crude oil and the heaviest residue left after distillation had the greatest effect on the wettability; they were the only fluids that made the rock oil-wet. This implies that a considerable portion of the surfactants in the crude oil had a large molecular weight. Many of the lower-molecular-weight fractions, however, also decreased the water-wettability, demonstrating that the surfactants in crude have a broad range of molecular weights. Cuiec⁹⁶ obtained similar results. Note that Denekas *et al.* and Cuiec both used dry cores and that adsorption of the wettability-altering compounds would probably have been altered if the cores contained brine during the aging process.

A number of researchers have examined the interfacially active materials that are concentrated at the oil/water interface. Generally, these materials can also be adsorbed on the rock surface to alter wettability.^{37,84,99-102} Bartell and Niederhauser¹⁰³ managed to separate these materials from the crude oil and found that they formed a hard, black, noncrystalline substance that was asphaltic in nature.

Adsorption Through Water Films. Experiments have shown that natural surfactants in crude are often sufficiently soluble in water to adsorb onto the rock surface after passing through a thin layer of water.^{42,60,69-71} Measurements comparing asphaltene adsorption in cores with and without water show that in many cases a water film will reduce but not completely inhibit asphaltene adsorption.^{60,69,70} Because the water and asphaltenes will coadsorb, however, the water film may alter the detailed adsorption mechanism.^{70,104} Lyutin and Burdyn⁶⁰ found that the asphaltene adsorption from Arlan crude in an unconsolidated sandpack was about 80% of the dry value at a water saturation of 10% PV, decreasing to 40% when the water saturation was increased to 30% PV. Berezin *et al.*⁶⁹ examined the adsorption of asphaltenes and resins from crude onto cleaned sandstone cores. With Tui-mazy crude, a water saturation of about 17% reduced the adsorption by about a factor of three. With two other crudes, a water saturation of about 20% completely inhibited the adsorption. Such complete inhibition by the water film would be expected in reservoirs that remain water-wet, with no significant adsorption from the crude.

Reisberg and Doscher⁶⁸ aged clean glass slides in crude oil floating above brine and observed the formation of oil-wet films. The formation and stability of the oil-wet film on the slide was observed by lowering the slide into the brine and observing whether the brine dis-

placed all of the crude oil from the slide. They first aged a clean glass slide in crude and found that a film, deposited over several days, made the slide moderately oil-wet. They modified the experiment by immersing the slide in water before aging it in crude. Surprisingly, the oil-wet film formed much more rapidly. When a NaCl solution was used instead of water, the slide also became oil-wet, but it was necessary to age the slide for a longer period of time.

Sandstone and Carbonate Surfaces. The types of mineral surfaces in a reservoir are also important in determining wettability. Both Treiber *et al.*³⁴ and Chilingar and Yen³⁵ found that carbonate reservoirs are typically more oil-wet than sandstone ones. Two other sets of experiments show that the mineral surface interacts with the crude oil composition to determine wettability. The first set examines the adsorption onto silica and carbonate surfaces of relatively simple polar compounds; the second set examines the adsorption of crude.

Simple Polar Compounds. When the effects of brine chemistry are removed, silica tends to adsorb simple organic bases, while the carbonates tend to adsorb simple organic acids.^{37,40,83} This occurs because silica normally has a negatively charged, weakly acidic surface in water near neutral pH, while the carbonates have positively charged, weakly basic surfaces.^{37,40,83,105}

These surfaces will preferentially adsorb compounds of the opposite polarity (acidity) by an acid/base reaction. Wettability of silica will be more strongly affected by the organic bases, while the carbonates will be more strongly affected by the organic acids. This was found to be the case in experiments on the adsorption and wettability alteration of relatively simple polar compounds on sandstone and carbonates. The compounds were dissolved in a nonpolar oil, and the contact angle of the oil/water/mineral system was measured on an initially clean, strongly water-wet crystal surface. Generally, adsorption and wettability alteration occurred with basic compounds on the acidic silica surfaces and acidic compounds on the basic carbonate surfaces. Acidic compounds had very little effect on silica, and basic compounds had little effect on the carbonates.^{37,40,42,56,78,79,106-109} Note, however, that most of the adsorbed compounds changed the wettability only from strongly to mildly water-wet, rather than to oil-wet.

The acidic compounds that adsorbed and altered the wettability of the carbonates in preference to silica included naphthenic acid^{37,109} and a number of carboxylic acids (RCOOH), including caprylic (octanoic),⁹⁶ palmitic (hexadecanoic),⁴² stearic (octadecanoic),^{106,108} and oleic (cis-9-octadecanoic) acids.⁴² Basic compounds that adsorbed on the acidic silica surfaces included isoquinoline³⁷ and octadecylamine [$\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$].^{106,108} Cram⁴⁰ and Morrow *et al.*⁶⁶ examined the adsorption and wettability alteration on quartz and dolomite of a number of relatively low-molecular-weight compounds found in crude oils. Basic nitrogen compounds gave advancing contact angles up to 66° [1.15 rad] (water-wet), with higher angles for quartz than dolomite. Sulfur compounds tested provided angles of 40° [0.7 rad] or less with no systematic differences between the two surfaces. The contact angles either were stable or decreased with time (i.e., the system became more water-wet). The acidic

oxygen compounds gave higher angles on dolomite than quartz, up to 145° [2.5 rad] for octanoic acid [$\text{CH}_3(\text{CH}_2)_6\text{COOH}$] and up to 165° [2.9 rad] for lauric acid [$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$]. Note, however, that the oxygen-containing acidic compounds appear to react gradually with the dolomite, so the contact angles are unstable and the system gradually becomes more water-wet. Cram *et al.* noted that none of the relatively simple compounds they tested could create a stable, oil-wet surface. Therefore, they concluded that the compounds responsible for wettability alteration in crude were higher-weight polar compounds and other portions of the asphaltenes and resins.

In the more complex crude/brine/rock systems, the mineral surface will not necessarily have a preference for compounds of the opposite acidity. The simple systems discussed here tested each surfactant individually and removed the effects of brine chemistry. In the section on brine chemistry, it will be shown that multivalent cations can promote the adsorption of surfactants with the same acidity as the surface. In addition, the adsorption of any single surfactant in the crude might be enhanced or depressed by the adsorption of other compounds.

Adsorption From Crude. A number of researchers found differences in the adsorption of crude oil components onto dry sandstone and carbonate surfaces.^{41,72-74,109,110} Denekas *et al.*⁴¹ separated out the acidic and basic organic compounds from crude and tested them in initially clean, dry cores by the method described earlier. They found that the wettability of sandstone was altered by both the acidic and basic compounds, while the limestone was more sensitive to the basic nitrogenous organic compounds.

Several experimenters have compared the adsorption of asphaltenes from crude onto initially clean, dry sandpacks composed of either quartz or disaggregated core material that contained both quartz and carbonate.^{72,110} They found that adsorption was greater in disaggregated core material. Tumasyan and Babalyan¹¹⁰ measured the adsorption of asphaltenes from Kyurovdag crude onto quartz and cleaned, disaggregated Kyurovdag core material that contained 10.4% carbonate. The adsorption was about 8×10^{-4} mg/cm² for quartz and about 18×10^{-4} mg/cm² for the core material, an increase of more than a factor of two. Abdurashitov *et al.*⁷² measured the adsorption of asphaltenes onto similar-sized fractions of pure quartz sands and sands containing both quartz and carbonate. They found that the adsorption on the quartz sands was as much as an order of magnitude lower than the adsorption on the sands containing both minerals. These results are very qualitative, however, because the specific surface area of the quartz packs was lower than the area of the mixed mineral sandpacks, which also reduces the amount of adsorption.

Brine Chemistry. The salinity and pH of brine are very important in determining wettability because they strongly affect the surface charge on the rock surface and fluid interfaces, which in turn can affect the adsorption of surfactants.^{80,105} Positively charged, cationic surfactants will be attracted to negatively charged surfaces, while negatively charged, anionic surfactants will be attracted to positively charged surfaces. The surface charge of silica and calcite in water is positive at low pH, but nega-

tive at high pH. For silica, the surface becomes negatively charged when the pH is increased above about 2 to 3.7,^{83,105} while calcite does not become negatively charged until the pH is greater than about 8 to 9.5.^{83,105,111} As discussed in the previous section, silica is negatively charged near neutral pH and tends to adsorb organic acids, while calcite is positively charged and tends to adsorb organic bases. Calcite will adsorb cationic surfactants rather than anionic surfactants, however, if the pH of the solution in which it is immersed is increased above 9.¹¹¹

The pH also affects the ionization of the surface-active organic acids and bases in the crude.⁸⁴ In alkaline water-flooding, a relatively inexpensive caustic chemical—typically sodium hydroxide or sodium orthosilicate—is added to the injection water.¹¹² The hydroxide ion reacts with organic acids in acidic crude oils to produce surfactants that alter the wettability and/or adsorb at the oil/brine interface to lower IFT. Seifert and Howells⁸⁵ examined the interfacially active materials in a California crude oil. They found that the crude contained a large amount of carboxylic acids that form soaps at alkaline pH.

The possibility of EOR during an alkaline flood depends on the pH and salinity of the brine, the acidity of the crude, and the original wettability of the system.^{26,113,114} Cooke *et al.*⁶ discussed the effects of salinity on wettability in alkaline floods where the soaps are formed by the interaction of the alkaline water with the acidic crude oil. In relatively fresh water, the soaps that are formed are soluble in water, promoting water-wetness. If the system is initially oil-wet, EOR may occur by a wettability reversal from oil-wet to water-wet.^{17,26,114,115} On the other hand, in high-salinity systems, EOR may occur as a result of a water-wet-to-oil-wet wettability reversal. As the salinity is increased, the soaps become almost insoluble, adsorb on the rock surfaces, and promote oil-wetting.^{6,113} If the system is initially water-wet, Cook *et al.* state that EOR in a highly saline system may occur by a water-wet-to-oil-wet wettability reversal mechanism.^{6,113,114}

In silica/oil/brine systems, multivalent metal cations in the brine can reduce the solubility of the crude surfactants and/or promote adsorption at the mineral surfaces, causing the system to become more oil-wet.^{6,34,77,79,81,116,117} Multivalent metal ions that have altered the wettability of such systems include Ca^{+2} , Mg^{+2} , Cu^{+2} , Ni^{+2} , and Fe^{+3} . Treiber *et al.*³⁴ examined the effects of trace metal ions in the brine on the wettability. They measured the contact angles on quartz of dead anaerobic crudes in deoxygenated synthetic formation brine and found that as little as 10 ppm of Cu^{+2} or Ni^{+2} could change the wettability from water-wet to oil-wet. Brown and Neustadter⁷⁷ placed crude oil droplets in a contact-angle apparatus filled with distilled water. They found that the addition of less than 1 ppm of Ca^{+2} or Mg^{+2} would alter the wettability, making the system more oil-wet. The addition of trace amounts of Fe^{+2} also changed the wettability with some of the crudes tested. These multivalent ions have also been shown to increase the oil wetness of soils stabilized with cut-back asphalt.^{118,119} (Cut-back asphalt is an asphalt treated with an inexpensive solvent, such as gasoline, to reduce the viscosity.) Hancock¹¹⁸ treated several strongly water-wet soils with cut-back asphalt. He found that the oil wetness

of the soil after the asphalt treatment was greatly increased by pretreating the soil with a solution of ferric or aluminum sulfate.

Morrow *et al.*⁸¹ aged glass slides in Moutray crude, washed the slides to remove the bulk crude, and then used isooctane and distilled water to measure the water-advancing angle. They found that the wettability strongly depended on the amount of trace ions in the system. When the glass slide was extremely clean, no residual film was deposited by the crude, and the system was water-wet. Next, they treated the glass with ferric (Fe^{+3}) or other transition metal ions before exposing it to the crude. They obtained contact angles up to 120 to 140° [2.1 to 2.4 rad], with the angle dependent on the choice of ion and its concentration. The ferric ion was particularly effective in altering the wettability.

There appear to be two related reasons for the effects of these multivalent ions on the wettability. First, they can reduce the solubility of the surfactants in the crude and brine, helping to promote oil-wetting.^{6,113} Second, they behave as "activators" for the surfactants in the crude. "Activator" is a term used in the flotation industry for ions or compounds that, while not surfactants themselves, enhance surfactant adsorption on the mineral surface and increase the floatability. Generally, the activators act like a bridge between the mineral surface and the adsorbing surfactant, helping to bind the surfactant to the surface.⁸⁰ As shown previously, clean quartz has a negatively charged surface and tends to adsorb (positively charged) organic bases from solution. The (negatively charged) acids in solution will not adsorb on the surface because they will be repelled by the like charge on the quartz surface. For example, clean quartz is not floated by fatty acids, indicating that the quartz remains water-wet. At the proper pH conditions, however, the wettability can be changed and the quartz can be floated by the addition of small amounts of many multivalent metallic cations, including Ca^{+2} , Ba^{+2} , Cu^{+2} , Al^{+3} , and Fe^{+3} .^{78,79,82,107} These ions adsorb on the quartz surface, providing positively charged sites for the adsorption of the fatty acids.

For example, Gaudin and Chang⁷⁸ and Gaudin and Fuerstenau⁷⁹ studied the adsorption of laurate ions on quartz. When sodium laurate, $\text{CH}_3(\text{CH}_2)_{10}\text{COONa}$, is added to the water, it dissociates into a negatively charged laurate ion and a positively charged Na^{+} ion. Because quartz develops a negative surface charge as a result of the dissociation of H^{+} ions from the Si-OH groups on the silica surface, the negatively charged laurate ion is repelled from the negatively charged quartz surface. Hence no adsorption occurs. However, adsorption occurs when, for example, divalent Ca^{+2} or Ba^{+2} ions are added as the activator. These positive divalent ions can adsorb on the surface, allowing the negatively charged surfactant (in this case, the laurate ions) to adsorb in association with them. Researchers with other experimental systems also state that divalent ions can bind to a negatively charged surfactant to form a positive, cationic surfactant/metal complex, which is then attracted to and adsorbs on the negatively charged quartz surface.^{116,117}

Clays. Several researchers have studied the adsorption of asphaltene and resins onto clays, and found that adsorption can make the clays more oil-wet.^{70,76,104,120-123}

Clementz^{104,120,121} examined adsorption under anhydrous conditions of the heavy ends—the nonvolatile, high-molecular-weight fraction—of crude oil, which are primarily asphaltenes and resins. He found that the compounds adsorbed rapidly onto montmorillonite, forming a stable clay/organic compound and changing the wettability from water-wet to oil-wet. Clementz also looked at adsorption under anhydrous conditions of the heavy ends onto Berea cores that contain significant amounts of kaolinite. The adsorption of the heavy ends made the core neutrally wet as determined by an imbibition test. The adsorption also reduced the expansion of swelling clays, clay surface area, cation exchange capacity, and water sensitivity. The materials that adsorbed onto both the montmorillonite and kaolinite were difficult to remove, although most of them could be extracted with a chloroform/acetone mixture.

Clementz used dry cores and clays. As discussed earlier, the presence of a water film will generally reduce the adsorption of wettability-altering materials, typically by a factor of two to four, although in some cases, it will completely inhibit adsorption.^{60,69} Collins and Melrose⁷⁰ measured the adsorption onto kaolinite of asphaltenes dissolved in toluene. The dry clay adsorbed a maximum of about 30 mg asphaltene/g clay. The addition of 6.6% water to the clay reduced the adsorption to 13 mg/g. In addition to reducing the adsorption, the water film may alter the detailed mechanism of asphaltene adsorption because the asphaltenes and water will coadsorb.⁷⁰ For example, in contrast to his work with anhydrous cores, Clementz found that the adsorption of asphaltenes onto Berea cores in the presence of water did not reduce the water sensitivity of the kaolinite.¹⁰⁴

Non-Water-Wet Minerals. When all of the surface contaminants are carefully removed, most minerals, including quartz, carbonates, and sulfates, are strongly water-wet.^{80,107,124} From flotation studies, however, a few minerals have been found that are naturally but weakly water-wet or even oil-wet. These minerals include sulfur, graphite, talc, coal, and many sulfides. Pyrophyllite and other talc-like silicates (silicates with a sheet-like structure) are probably also neutrally wet to oil-wet.^{80,107,124-127} These minerals are known to be somewhat hydrophobic because air can be used to float them on water in froth flotation, implying a large water/air/mineral contact angle. Because they are non-water-wet with air, it is probable that they are also oil-wet.

On the basis of core-cleaning attempts in a limited number of reservoirs, it appears that cores containing coal are sometimes naturally neutrally wet because they can be cleaned only to a neutrally wet condition rather than a strongly water-wet one.^{128,129} Cuiec⁹⁶ and Cuiec *et al.*¹³⁰ cleaned unpreserved cores with different solvents and then measured wettability. In four cases where cores contained large amounts of unextractable organic carbon, they were able to clean the cores only to neutral wettability. Wendel *et al.*¹²⁸ cleaned core from the Hutton reservoir contaminated with an invert-oil-emulsion drilling mud. Core from most zones in this reservoir could be cleaned to a water-wet state. However, in one zone that contained significant amounts of coal, the core was neutrally wet after cleaning. About 50% of the rock surface in the neutrally wet zone was covered by a thin layer of organic matter less than 300 Å [30 nm] thick. This layer

may be a result of diffusion of organic compounds released during diagenesis from the small, organic, detrital particles of coal scattered throughout the zone. Unfortunately, this is unclear at present. Thin sections from both water-wet and neutrally wet (after cleaning) zones show that both contain approximately equal amounts and distribution of woody coal, algae coal, and pyrite. Consequently, it is unknown what causes the postcleaning neutral wettability of this neutrally wet zone.

Boneau and Clampitt¹³¹ and Trantham and Clampitt¹³² state that the oil wetness of the North Burbank unit is caused by a coating of chamosite clay ($\text{Fe}_3\text{Al}_2\text{Si}_2\text{O}_{10} \cdot 3\text{H}_2\text{O}$) on the pore surfaces rather than the more common, strongly adsorbed organic coating. The chamosite clay, which is iron rich, covers about 70% of the rock surfaces. It seems plausible that the chamosite clay renders the core oil-wet because, as discussed earlier, iron ions are strong activators, promoting oil-wetting. Clampitt* states that unpublished contact-angle measurements made with all of the minerals in the North Burbank core showed that chamosite is naturally oil-wet.

Artificial Variation of Wettability

As described previously, a native-state core contains a complex mixture of different compounds that can adsorb and desorb, possibly altering the wettability during an experiment. Many researchers have tried to simplify their experiments by artificially controlling the wettability to some constant, uniform value. The three methods most commonly used are (1) treatment of a clean, dry core with various chemicals, generally organochlorosilanes for sandstone cores and naphthenic acids for carbonate cores; (2) using sintered cores with pure fluids; and (3) adding surfactants to the fluids. A sintered teflon core with pure fluids is the preferred method to obtain a uniformly wetted core because the wettability of these cores is constant and reproducible. The wettability of cores treated with organochlorosilanes, naphthenic acids, or surfactants is much more variable because it also depends on such variables as the chemical used, the concentration, the treatment time, the rock surface, and the brine pH. These treatments have advantages, however, when heterogeneous wettability or wettability alteration is studied.

Organochlorosilanes and Other Core Treatments. One method of making a sandstone core uniformly non-water-wet is to treat it with a solution containing an organochlorosilane compound.¹³³⁻¹³⁹ Variations of this treatment have also been used to create fractionally wetted sandpacks^{43,46,50,140-142} and mixed-wet cores.¹⁴³ The organosilane compounds contain silicon molecules with attached chlorines and non-water-wet organic groups, with the general formula $\text{R}_n\text{SiCl}_{4-n}$ where R is usually methyl or phenyl and $n=0, 1, 2, \text{ or } 3$.¹³³ These substances react with the hydroxyl (OH) groups on silicon dioxide surfaces, exposing the organic groups and rendering the surface non-water-wet. For example, dimethyldichlorosilane, $(\text{CH}_3)_2\text{SiCl}_2$ (Drifilm® or Teddol®), chemisorbs on the outside of the silicate lattice of glass, eliminating HCl and exposing CH_3 groups, which reduce the water-wetness of the surface.¹⁴⁴ Other compounds include hexamethyldisilazane¹³⁸ and trimethylchlorosilane.¹⁴⁵ The wettability of the core is altered by flowing

*Personal communication with R.L. Clampitt, Phillips Petroleum, Bartlesville, OK, Dec. 1985.

a solution of the organosilane through it, allowing a sufficient time for the reaction to occur, and then flushing the unreacted compound from the core. Some control of the change in wettability can be achieved by variation in the concentration of organosilane in the solution. For a complete description of the method, see Ref. 134.

In addition to uniformly treating cores, organochlorosilanes are used to prepare fractionally wetted sand-packs.^{43,46,50,140-142} Sand grains treated with organochlorosilanes are mixed with untreated, water-wet sands. The fraction of oil-wet surface is assumed to be the same as the fraction of organochlorosilane-treated sand. One problem, however, is that some of the organochlorosilane is known to be transferred to the water-wet sand grains, likely changing their wettability.⁴³ Another method of obtaining fractional wettability is to form the porous medium from water-wet (glass) beads and oil-wet (teflon) beads.¹⁴⁶

Mohanty and Salter¹⁴³ have recently published a technique to generate mixed-wettability cores so that the large pores have continuous water-wet surfaces, leaving the small pores oil-wet. Note that in these cores, the wettability is reversed from Salathiel's⁴⁷ mixed-wettability cores. Cleaned cores are first treated with organosilanes to render them uniformly oil-wet. The treated cores are saturated with oil, flooded with heptadecane to displace the oil, and then flooded with brine to ROS. Because the core is oil-wet, the large pores are filled with brine, but the small ones are filled with oil. Brine and heptadecane may then be injected simultaneously to alter the fraction of pores filled with oil or water. After the desired saturation is reached, the core is first placed in a cold water bath (50°F [10°C]) to freeze the heptadecane, then an 11.5 pH sodium hydroxide solution is injected to displace the brine. Mohanty and Salter state that the alkaline solution removes the organosilane coating from the larger, brine-filled pores, leaving them strongly water-wet, while the frozen heptadecane prevents any change in wettability in the small oil-filled, oil-wet pores. Finally, the alkaline solution is displaced with brine, and all of the fluids are removed, leaving a mixed-wettability core. After this treatment, the cores imbibed both oil and water, indicating that areas of the core were both water- and oil-wet. Unfortunately, Mohanty and Salter did not test the cores by oil flooding them to determine whether they had a very low water saturation after the injection of many PV's of oil. This would have verified the formation of continuous water-wet paths through the large pores, which would be analogous to oil-wet paths in Salathiel's cores.

One problem with organochlorosilane treatments is that the wettability of the treated core varies depending on such variables as the organochlorosilane used, the concentration, the treatment time, the time elapsed since the surface was treated, and the pH of the brine.¹⁴⁷ No dependable treatment has been reported for achieving a given core wettability. Note that many organosilane-treated cores are only neutrally to mildly oil-wet, instead of strongly oil-wet. Coley *et al.*¹³⁴ used General Electric Co. silicone fluid No. 99 in concentrations ranging from 0.002 to 2.0% and were able to vary the contact angle in glass capillaries only from 95 to 115° [1.7 to 2 rad]. Rathmell *et al.*¹³⁷ found that cores treated with dimethyldichlorosilane would still slowly imbibe water, indicating that the cores were at most neutrally wet. In

contrast, Newcombe *et al.*¹³⁶ stated that contact angles as large as 154° [2.7 rad] could be obtained for silica surfaces treated with different concentrations of methylsiloxane polymer, but these contact angles tended to decrease toward 90° [1.6 rad] as they aged. Menawat *et al.*¹⁴⁸ treated silica surfaces with various concentrations of four different organochlorosilanes and obtained contact angles from 75 to 160° [1.3 to 2.8 rad] with water and xylene on the treated surfaces. Depending on the specific treatment, they found that the contact angle could gradually increase or decrease as the system aged. Because the wettability of cores treated with organosilanes can range from mildly water-wet to strongly oil-wet depending on the specific treatment, the Amott or USBM method should be used to determine the wettability of the treated core.

Quilon® treatments are another method that has been used to alter the wettability of sandstone cores. Tiffin and Yellig¹⁴⁹ treated Berea cores with Quilon-C® to render them uniformly oil-wet. Workers at the Petroleum Recovery Inst. have used Quilon-S®, a related compound.¹⁵⁰⁻¹⁵³ The Quilon compounds consist of a chrome complex containing a hydrophobic fatty acid group in an isopropyl alcohol solution. When Quilon is injected into the core, the molecules bind to the surface, expose the fatty acid group, and render the rock surface oil-wet.¹⁵⁴ Note that wettability of the treated core probably varies, depending on concentration, treatment time, etc., so it should be measured with the USBM or Amott methods. In many cases, the treated core is probably only neutrally to mildly oil-wet.

These treatments have been used on sandstone core with the chemical binding to the silica surfaces. Organochlorosilane treatments, which adsorb on silica surfaces by reacting with the hydroxyl groups, are generally not effective on carbonate surfaces.^{155,156} A number of researchers^{109,155-157} have used naphthenic acids to render carbonate cores more oil-wet.³⁷ The naphthenic acids react with the calcium carbonate to form calcium naphthenates, which are oil-wetting.¹⁰⁹ Note that naphthenic acids will not alter the wettability of sandstone surfaces.¹⁰⁹

Sharma and Wunderlich¹⁵⁸ altered the wettability of Berea plugs by saturating them with an asphaltic crude. Dry plugs were vacuum-saturated with asphaltic crude oil, then flushed with pentane, which tends to precipitate asphaltenes onto the pore walls.⁶⁷ The pentane was removed in a vacuum, leaving behind a layer of asphaltenes. The plugs probably had mixed wettability after treatment; both oil and water would imbibe spontaneously.³ An advantage of this method is that it uses compounds found naturally in the reservoir and might be a more realistic treatment than the other treatments discussed above. Note, however, that it is necessary to verify that the crude is compatible with the pentane because some crudes will plug the core when pentane is injected.

Artificial Cores. Several researchers have used artificial cores and pure fluids to control wettability. The uniform composition of the core and the absence of surfactants combine to give a constant, uniform, and reproducible wettability. The most popular material for the artificial core has been polytetrafluoroethylene (teflon). Stegemeier and Jessen¹⁵⁹ used porous packs of teflon particles. More recent experiments have used consolidated teflon

cores,¹⁶⁰⁻¹⁶⁸ which are prepared by compressing teflon powder and sintering it at elevated temperatures to produce a consolidated core. Mungan¹⁶⁷ completely describes the process. Lefebvre du Prey¹⁶⁰ has also used sintered stainless steel and alumina cores.

Teflon is preferred for two reasons: it is chemically inert and has a low surface energy.¹⁶⁹ Most minerals found in reservoir rock have a high surface energy, so almost all liquids will spread on and wet them against air. The wettability of such high-energy solids must be controlled with either adsorbed films on the solid surface or surfactants in the fluids. Both of these methods raise the problem of changes in the wettability during the experiment as a result of adsorption/desorption phenomena. On the other hand, the surface energy of teflon is low enough that a wide range of contact angles can be obtained with various combinations of pure fluids that do not contain surfactants. The use of pure fluids with teflon also avoids difficulties with contact-angle hysteresis associated with adsorption/desorption equilibrium and the problems associated with contact angle and IFT aging phenomena. This is discussed in more detail in Ref. 1. Many experiments in teflon cores use air or N₂ and various fluids to vary the contact angle. Contact angles from 0 to 108° [0 to 1.9 rad] can be obtained by the proper choice of liquid/gas pairs.¹⁶¹ For example, an air/water/teflon system has a contact angle through the water of 108° [1.9 rad]. Lefebvre du Prey¹⁶⁰ used mixtures of water, glycerol, glycol, and alcohols to represent the water phase and mixtures of pure hydrocarbons for the oil phase. Contact angles through the oil phase of from 0 to 168° [0 to 2.9 rad] were reported for his teflon, steel, and alumina cores.

Surface-Active Agents. The use of clean cores and pure fluids with various concentrations of a single surfactant is the third way that researchers have controlled the wettability of cores. Owens and Archer²⁸ used barium dinonyl sulfonate in the oil and reported stable contact angles up to 180° [3.1 rad] on a quartz crystal. Morrow *et al.*⁶⁶ were unable to reproduce this work, finding a strong time dependence for the contact angle. They tried to control the wettability with octanoic acid, obtaining angles from 0 to 155° [0 to 2.7 rad] on dolomite. They found that the wettability could be maintained for less than a day, however, after which the system became increasingly water-wet as the octanoic acid slowly reacted with the dolomite.

A number of researchers^{17,26,170-174} have used amines, R-NH₂, to study EOR caused by wettability alteration in laboratory waterfloods. Wettability reversal from oil-wet to water-wet and from water-wet to oil-wet are two of the proposed mechanisms for enhanced recovery during alkaline waterflooding.¹¹⁴ In these laboratory studies, clean core, a refined oil, and a brine containing amines were used. The wettability was reversed by changing the pH from alkaline to acidic. When the pH was alkaline, the amine group physically adsorbed on the rock surface, exposing the hydrocarbon chain to make the surface oil-wet.¹⁷³ The wettability was altered when the pH became acidic because the amines formed water-soluble salts that rapidly desorbed from the rock surfaces, leaving them water-wet. Hence a core that is oil-wet becomes water-

wet when water containing a mild acid is injected. The most commonly used amines have been hexylamine and n-octylamine. Mungan¹⁷⁴ measured the water-advancing contact angle on a silica surface using water, n-hexylamine, and a refined oil. The contact angle with no amines present was about 60° [1 rad], or water-wet. As the concentration of amines was increased, the contact angle gradually changed to about 120° [2.1 rad], or mildly oil-wet. In addition to altering the wettability, the amines partition between the oil and water and lower IFT.

Alteration of the Original Wettability

As mentioned previously, alterations in wettability can affect the results of most core analyses. Ideally, these analyses should be run with core wettability that is identical to the wettability of the undisturbed reservoir rock. Unfortunately, many factors can significantly alter the wettability of the core. These factors can be divided into two general categories: (1) those that influence core wettability before testing, such as drilling fluids, packaging, preservation, and cleaning; and (2) those that influence wettability during testing, such as test fluids, temperature, and pressure.

The wettability of a core can be altered during the drilling process by the flushing actions of drilling fluids, particularly if the fluid contains surfactants^{128,175} or has a pH^{77,114,176} different from that of the reservoir fluids. The wettability may also be changed by the pressure and temperature drop that occurs as the core is brought to the surface. This action expels fluids, particularly the light ends, and changes the spatial distribution of the fluids. In addition, asphaltenes and other heavy ends may deposit on the rock surfaces, making them more oil-wet. The techniques used in handling, packaging, and preserving the core can also alter the wettability through a loss of light ends, deposition of heavy ends, and oxidation. The laboratory procedures for cleaning and preparing the core can change the wettability by altering the amount and type of material adsorbed on the rock surface.

Factors that can alter wettability during testing include the test temperature and pressure. Generally, cores run at atmospheric conditions are more oil-wet than those run at reservoir conditions because of the reduction in solubility of wettability-altering compounds. An additional factor influencing the wettability is the choice of test fluids; certain mineral oils can alter the wettability. Core analyses are sometimes run with air/brine or air/mercury in place of oil and brine. These analyses implicitly assume that wettability effects are unimportant.

Currently, three different types of cores are used in core analysis: (1) the native-state core, where every effort is made to maintain the wettability of the in-situ rock; (2) the cleaned core, where the intent is to remove all of the adsorbed compounds from the rock and to leave the core strongly water-wet; and (3) the restored-state core, where the core is first cleaned and then returned to its original wettability. These definitions are used in the majority of the more recent literature. However, in some papers, particularly older ones, the term restored-state is used for what are actually cleaned cores (e.g., see Craig⁷). The work with native- and restored-state core is at either ambient or reservoir temperature and pressure, while cleaned cores are usually tested at ambient temperature.

Native-State Core

Coring. In a native-state (fresh) core, every precaution is taken to minimize changes from the undisturbed reservoir wettability condition, starting when the core is first flushed by the drilling mud. In particular, a mud with surfactants or a pH that differs greatly from the reservoir fluids must be avoided. Oil-based-emulsion muds and other muds containing surfactants, caustics, mud thinners, organic corrosion inhibitors, and lignosulfonates must be avoided.^{175,177} Note that, while they probably exist, no commercially available oil-based muds have been reported that can preserve the reservoir wettability.^{175,177,178}

Three different coring fluids for obtaining native-state core have been recommended: (1) synthetic formation brine, (2) unoxidized lease crude oil, or (3) a water-based mud with a minimum of additives. Bobek *et al.*¹⁷⁵ recommend coring with brine and no additives. If this is not possible, a water-based mud containing only bentonite, carboxymethyl cellulose, rock salt, and barite should be used. This is recommended because they found that this would not alter the wettability of strongly water-wet cores. Note, however, that the carboxymethyl cellulose may alter the wettability of oil-wet cores, rendering them more water-wet.^{158,175} Ehrlich and Wygal¹⁷⁹ recommend a synthetic formation brine containing CaCl_2 powder for fluid loss control and no other additives. Mungan¹⁸⁰ recommends coring with lease crude oil. Note that there are two possible problems with the use of crude oil: (1) it is flammable, and (2) surfactants can be formed by oxidation of the crude, which could alter the wettability.^{34,103}

Unfortunately, very little work has been published about the effects of individual drilling mud components on wettability, particularly for oil-wet cores. Burkhardt *et al.*¹⁷⁶ examined the effects of mud filtrate flushing on restored-state cores and found no significant effects. Unfortunately, the cores were in contact with the crude oil for only 12 to 16 hours, so it is doubtful that the wettability was restored before testing.

Bobek *et al.*¹⁷⁵ tested several different drilling mud components used in water-base muds on both water-wet and oil-wet plugs. The drilling mud components to be tested were dissolved in or leached with distilled water; then the resulting solution was filtered. Concentrations of the compounds were chosen to duplicate those encountered in the field. Water-wet limestone and sandstone plugs were saturated with the test solution and wettability alteration monitored by the imbibition method. As discussed earlier, they found that rock salt, carboxymethyl cellulose, bentonite, and barite had no effect on the wettability of these initially water-wet plugs. Starch, lime, tetrasodium phosphate, and calcium lignosulfonate altered the wettability of the sandstone and/or limestone plugs.

Drilling components that did not affect the water-wet plugs were tested on oil-wet sandstone plugs. The dry, initially water-wet plugs were made oil-wet before testing by saturation with Elk Basin crude and aging for one day. Note that because of the short duration of the aging, the wettability may not have been in equilibrium. The aged cores were flushed with a drilling mud component filtrate; then the wettability was measured by the imbibition method. Salt did not affect the wettability, while carboxymethyl cellulose made the plugs more water-wet (barite was not tested). Bobek *et al.* found that the pH

of the filtrates was an important factor in wettability alteration. The original bentonite filtrate changed the wettability from oil-wet to water-wet. When the pH was lowered into the neutral or acidic range, however, no wettability reversal occurred.

Sharma and Wunderlich¹⁵⁸ measured the wettability alteration caused by different drilling mud components in water-wet and oil-wet Berea plugs. The oil-wet Berea plugs were prepared by treatment with an asphaltic crude and pentane, as discussed previously. Dry plugs were saturated with brine, injected with 10 to 12 PV's of the drilling fluid component, aged for 15 hours, then flushed with 5 to 6 PV's of brine. Wettability was measured after contamination by a combined USBM/Amott method developed by Sharma and Wunderlich¹⁵⁸ and compared with the wettability of control samples. The drilling components tested included bentonite, carboxymethyl cellulose, Dextrid® (an organic polymer), Drispac® (a polyanionic cellulose polymer), hydroxyethylcellulose, pregelatinized starch, and xanthan gum. These components are generally considered relatively bland, with only small effects on the wettability. None of the components affected the wettability of the water-wet plugs. However, all of the components, with the exception of the bentonite filtrate, made the oil-wet plugs significantly less oil-wet. This indicates the need for further research on acceptable drillings muds for obtaining native-state core.

Several researchers have attempted unsuccessfully to find suitable commercially available oil-based muds for obtaining native-state core.^{175, 177, 178} All of the oil-based drilling mud filtrates tested made water-wet cores more oil-wet. Unfortunately, none of the reports identify the specific drilling mud components used.

Core Packaging and Preservation. Once the core is brought to the surface, it must be protected from wettability alteration caused by the loss of light ends or deposition and oxidation of heavy ends. On exposure to air, substances in crude can rapidly oxidize to form polar products that are surfactants, altering the wettability.^{34,73,103,115,175,181,182} In addition, a thick oil-wet residue from the crude will be deposited on the rock surface if the core is allowed to dry out. To prevent wettability alteration, Bobek *et al.*¹⁷⁵ recommended two alternative packaging procedures that are now generally used for native-state cores. The first is to wrap the cores at the wellsite in polyethylene or polyvinylidene film and then in aluminum foil. The wrapped cores are then sealed with a thick layer of paraffin or a special plastic sealer designed to exclude oxygen and prevent evaporation. The second, preferred method is to immerse the cores at the wellsite in deoxygenated formation or synthetic brine in a glass-lined steel or plastic tube, which is then sealed to prevent leakage and the entrance of oxygen. Imbibition wettability tests showed that the wettability of core packaged by either of these two methods was unchanged from the wettability measured at the wellsite. Instead of deoxygenated brine, Mungan¹⁸⁰ recommended that the cores be cut and stored in degassed lease crude oil. Morgan and Gordan¹⁸³ and McGhee *et al.*⁶² recommended that the cores be stored in their wetting fluid, either formation brine or crude oil. The wettability would be determined by an imbibition test at the wellsite. Finally, note that cores taken in a rubber sleeve, fiberglass, or PVC

TABLE 3—EFFECTS OF EXPOSURE TO AIR AND PARTIAL DRYING ON
NATIVE-STATE CORE

Number of Cores Tested	Description	Average Displacement- by-Water Ratio	Average Displacement- by-Oil Ratio
2	Native state	0.97	0.00
3	Exposed to air at 70 to 100°F for 1 day	0.63	0.00
2	Exposed to air at 75°F for 60 days	0.42	0.00
4	Exposed to air at 225°F for 7 days	0.18	0.00

Data obtained by use of the Amott wettability test, native-state core from Oil Zone B., Sterling County, TX.¹⁷⁷

liner can be preserved if the ends are capped and sealed.

A number of experiments have demonstrated that exposure to air and drying can alter the wettability of core. As discussed earlier, Treiber *et al.*³⁴ measured the wettability of 50 reservoirs using deoxygenated synthetic formation brine and anaerobic crude. In some cases, the contact angle showed that the reservoir was water-wet. For some of those crudes, exposure to oxygen changed the wettability to oil-wet. Bartell and Niederhauser¹⁰³ studied interfacially active materials in crude, which concentrate and form solid films at the oil/water interface. These materials can also be adsorbed on the rock surface, rendering it oil-wet. Crudes and brines were obtained and stored without exposure to oxygen. Most of these crudes showed very little interfacial activity. On exposure to air, the crudes developed moderate-to-strong film-forming tendencies, while the oil/water IFT was lowered by as much as 50%, indicating that surfactants were formed by oxidation of the crude.

Richardson *et al.*¹⁸² stored core from a mixed-wettability reservoir⁴⁷ using four different methods. Oxidation and drying of the core were prevented with the first two methods: (1) core wrapped in foil and sealed in paraffin and (2) core stored in evacuated (deoxygenated) formation water. The other methods were (3) core stored in aerated formation water and (4) core stored in cloth core bags. The cores were oilflooded with kerosene to IWS and then waterflooded. The average ROS for the samples protected from oxidation and drying (Methods 1 and 2) was about 13%; for the samples submerged in aerated water, about 24%; and for the samples stored in core bags, about 25%.

Bobek *et al.*¹⁷⁵ used the imbibition method to compare the wettability of native-state cores at the wellsite, cores allowed to weather, and cores stored by the two recommended methods discussed above. The wettability of the cores stored by either of the two recommended methods was the same as the wettability measured at the wellsite, while most of the weathered cores became more oil-wet.

Amott¹⁷⁷ used his method to compare the wettability of native-state cores with similar cores that were exposed to oxygen and allowed to partially dry, as shown in Table 3. The native-state cores were strongly water-wet, with a displacement-by-water ratio of 0.97. In the Amott test, the displacement-by-water ratio is the ratio of the oil volume displaced by spontaneous imbibition to the total oil volume displaced by both imbibition and forced displacement. It is zero for neutrally and oil-wet cores and

approaches one as the water-wetness increases. Similarly, the displacement-by-oil ratio is zero for neutrally and water-wet cores and approaches one as the oil-wetness increases. The cores became more oil-wet as they were either exposed to the air for longer periods of time, or at higher temperatures. Similar tests on an initially weakly water-wet core showed almost no change. On the other hand, Mungan¹¹⁵ used the imbibition method to measure the wettability of native-state cores. In contrast to the experiments discussed above, cores preserved in deaerated water were oil-wet, but became water-wet when exposed to air for 1 week. Chilingar and Yen³⁵ have also reported that some cores became more water-wet on exposure to air, indicating that it is impossible to predict how the wettability will be altered by the oxidation of the crude.

Mungan¹⁸⁰ recommends flushing native-state core with live crude oil before any flow studies are started. After native-state cores have been prepared, they are usually run at reservoir conditions with crude oil and brine.

Probably the greatest, uncontrollable problem with native-state core is the alteration of wettability as the core is brought to the surface. When the pressure is lowered to atmospheric, light ends are lost from the crude, changing its properties. In addition, heavy components can come out of solution and deposit on the rock, making it more oil-wet.¹³⁷ The decrease in temperature will also decrease the solubility of some wettability-altering compounds. Pressure coring prevents the loss of light ends. However, the cores are frozen before removal, so wettability-altering compounds can deposit. Unfortunately, there is no experimental work available on wettability alteration as the core is brought to the surface.

Cleaned Core

The second type of core used in core analysis is the cleaned core. Craig⁷ recommends that cleaned core be used for multiphase flow measurements only when the reservoir is known to be strongly water-wet because errors in the core analysis will be introduced otherwise. There are two main reasons to clean core. The first is to remove all liquids from the core so that porosity, permeability, and fluid saturations can be measured. Core cleaning for these routine core measurements will not be considered in this paper. The second reason for cleaning is to obtain a strongly water-wet core, generally as a first step in restoring the wettability of a contaminated core.

In obtaining a cleaned core, an attempt is made to remove all of the fluids and adsorbed material, leaving a clean rock surface. Gant and Anderson¹²⁹ discuss the methods used to clean core. One common method is reflux extraction (Dean-Stark or Soxhlet) with a solvent such as toluene, sometimes followed by extraction with chloroform or methanol. Alternatively, a flow-through system where the solvents are injected under pressure is sometimes used.^{57,64,65} If the cleaning procedure is successful, the core is left strongly water-wet. Cuiec^{64,65} and others^{57,184} discussed the chemical reactions involved in the cleaning process.

Cuiec^{64,65} compared the efficiency of different solvents in flow-through core cleaning. Initially water-wet outcrop sandstone and limestone cores were saturated with different crudes (sometimes the cores also contained brine), then aged. The aged cores were normally neutral- to oil-wet, as determined by the Amott wettability test. The cores were then cleaned with different solvents, and the Amott test was used to determine cleaning efficiency. Cuiec found that he could clean both sandstone and limestone cores by flowing the following seven solvents through the core: pentane, hexane, heptane, cyclohexane, benzene, pyridine, and ethanol. Chloroform, toluene, and methanol used singly were not very effective. Cuiec also looked at several different acidic and basic solvents used individually and found that the acidic solvents tended to be more effective in cleaning sandstone, while the basic solvents were better in cleaning limestone. This difference was attributed to the acidic nature of the sandstone surface and the basic nature of the limestone surface. For example, because sandstone (silica) has a weakly acidic surface, it tends to adsorb bases from the crude oil. When a stronger acid flows through the system, it will gradually react with and strip off the adsorbed bases, leaving a clean silica surface.

Gant and Anderson¹²⁹ surveyed most of the core-cleaning experiments in the literature. They found that the best choice of solvents depends heavily on the crude and the mineral surfaces because they help determine the amount and type of wettability-altering compounds adsorbed. Solvents that give good results with some cores and crudes often fail in other cases. For example, Grist *et al.*¹⁸⁴ and Holbrook and Bernard⁴⁵ both found that they could clean core to a strongly water-wet state using a chloroform/methanol mixture, while Jennings⁵⁸ reported that this was unsuccessful. For cleaning for routine core analysis, API¹⁸⁵ reports that chloroform is excellent for many midcontinent crudes, while toluene is useful for asphaltic crudes.

In many cases, it appears that any single solvent is relatively ineffective in core cleaning and that much better results can be obtained with a mixture or series of solvents.¹²⁹ The following solvents have been reported for specific combinations of crude and core to give poor results when used alone: chloroform,^{64,65} benzene,^{58,104,120} carbon disulfide,^{104,120} ethanol,⁶⁴ and toluene.^{58,64,65,104,120,177,184,186}

Many of the researchers cited above have found that toluene used alone is one of the least effective solvents. However, when combined with other solvents, such as methanol (CH_3OH)¹⁸⁴ or ethanol ($\text{CH}_3\text{CH}_2\text{OH}$),⁶¹ toluene is often very effective. The toluene is effective in removing the hydrocarbons, including asphal-

tenes^{130,185} and some of the weakly polar compounds,¹⁸⁴ while the more strongly polar methanol (ethanol) removes the strongly adsorbed polar compounds that are often responsible for altering wettability. In addition to toluene/methanol and toluene/ethanol, successful cleaning has also been reported with chloroform/acetone^{104,120,123} and chloroform/methanol,¹⁸⁴ as well as a number of different series of solvents.^{64,65}

Cuiec and his coworkers made the most extensive study of core cleaning for wettability restoration. In a recent paper, Cuiec *et al.*¹³⁰ stated that their core cleaning always begins with a toluene flush to remove hydrocarbons and asphaltenes. A number of solvents are then tested to determine the most effective, including (1) a series of non-polar solvents, e.g., cyclohexane or heptane; (2) acidic solvents, e.g., chloroform, ethanol, or methanol; (3) basic solvents, e.g., dioxane or pyridine; and (4) mixtures of solvents, e.g., methanol/acetone/toluene. When none of these procedures are effective, other tests are performed by combining the above procedures, using other solvents, and increasing the circulation time.

Toluene is generally not a very effective solvent, but it can alter the wettability of some core. Jennings¹⁸⁶ cleaned several cores by toluene extraction and found that the wettabilities and relative permeabilities were not changed. He stated that this indicated that toluene-extracted core retained the reservoir wettability and could be used for relative permeability measurements. However, this generally is not the case. Although it is less efficient than other solvents, we have found that toluene extraction can alter the wettability and relative permeabilities of native-state core. In some cases, neutrally wet or mildly oil-wet native-state core becomes strongly water-wet after extraction with toluene. The relative permeability curves also shift. Amott¹⁷⁷ also found that toluene extraction can clean some cores, while it had little effect for other ones, such as the strongly oil-wet Bradford cores. Therefore, because toluene extraction will alter the wettability and relative permeability of many native-state cores, measurements should be made on native-state cores before toluene extraction.

One problem with a cleaned core is that it is sometimes difficult, if not impossible, to remove all of the adsorbed material. If this occurs, the wettability of the cleaned core will be left in some indefinite state, causing variations in core analyses. Grist *et al.*¹⁸⁴ cleaned cores by three currently used methods and then examined how ROS and endpoint effective permeabilities varied after a waterflood. ROS was very similar for all methods. However, the endpoint effective water permeability varied by more than a factor of three between different cleaning methods. Their explanation for this behavior was that some methods were able to extract more of the adsorbed components, leaving the rock more water-wet. In the more water-wet cores, the residual oil had a greater tendency to form trapped droplets, blocking pore throats and lowering water permeability. The least effective of the three cleaning methods was overnight reflux extraction with toluene. More effective was reflux extraction with toluene followed by 2 days of extraction with a mixture of chloroform and methanol. Finally, the most efficient method was reflux extraction with toluene followed by 3 weeks of extraction with chloroform and methanol. In the last stage of cleaning, methanol was used alone.

Another drawback of cleaned cores is that it is occasionally possible for cleaning to change an originally water-wet rock to an oil-wet one. The extraction process may quickly boil off the connate water, allowing the remaining oil to contact the rock surface and form oil-wet deposits that are almost impossible to remove.¹⁸⁷

The cleaning experiments discussed examine the best methods to remove crude oil constituents from the pore walls. In many cases, core is also contaminated with drilling mud surfactants, which must also be removed before the wettability of a core can be restored.^{128,129} The best choice of solvents depends on the crude, the mineral surfaces, and the drilling mud surfactants. Gant and Anderson¹²⁹ cleaned Berea sandstone and Guelph (Baker) dolomite plugs contaminated with an invert-oil-emulsion drilling mud filtrate. The best solvent for both rock types was a 50/50 mixture of toluene/methanol, or the equivalent, containing 1% ammonium hydroxide. A three-step method (three successive Dean-Stark extractions—toluene, followed by glacial acetic acid, followed by ethanol) was the second best choice for Berea, while 2-methoxyethyl ether was the second best choice for dolomite, demonstrating that the choice of solvents can depend on the mineral surfaces in the core.

Restored-State Core

If one could be positive that the original reservoir wettability had not been inadvertently modified, a native-state core would give results closest to those of the reservoir. However, native-state cores present several problems. The necessary procedures to preserve the wettability are troublesome and time-consuming. Even when all of the precautions are taken, there is still a possibility that the wettability has been changed through oxidation or through deposition as the temperature and pressure dropped when the core was brought to the surface. In addition, the question arises about the procedure to follow to obtain the most reliable information from cores in which the wettability was altered.

When only core with altered wettability is available, the best possible multiphase measurements are obtained by restoring the reservoir wettability with a three-step process.^{47,50,64,65,96,115,128,130,180,188} The first step is to clean the core to remove all compounds from the rock surface. After the core is cleaned, the second step is to flow reservoir fluids into the core sequentially. Finally, the core is aged at the reservoir temperature for a sufficient time to establish adsorption equilibrium. Several experimenters have compared measurements made on core in the native, cleaned, and restored states. In each experiment, measurements in the restored state were almost identical to the previous native-state ones, demonstrating that this procedure will restore wettability.^{50,115,180,188}

The first and most difficult step in wettability restoration is to clean the contaminated core by use of the methods described to remove all compounds adsorbed on the surfaces and to make the core as water-wet as possible. All compounds must be removed from the core because we have no knowledge of which compounds were adsorbed on the undisturbed reservoir rock and which were deposited afterward. The USBM or Amott wettability measurements are used to verify that the core is strongly water-wet. Unfortunately, determining which solvent will successfully clean the core is still a trial-and-

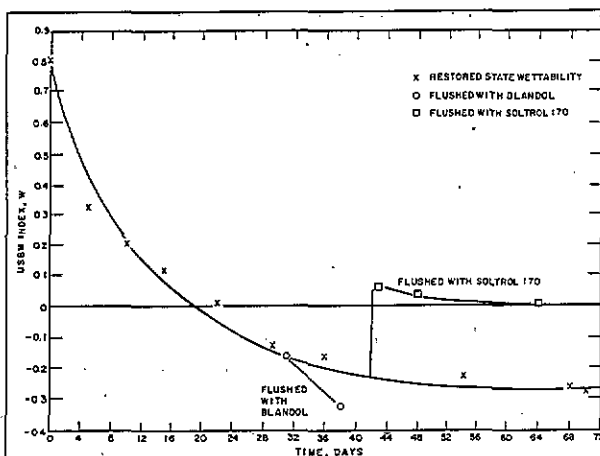


Fig. 1—Wettability changes for a restored-state core and the effects of flushing restored-state cores with refined oils. Berea core and Big Muddy crude.

error process because the best choice of solvents depends heavily on the crude oil, the mineral surfaces, and any drilling mud contaminants. Further discussion can be found in Ref. 129.

In the second step, sequentially flowing reservoir fluids into the core, the core is saturated with deoxygenated synthetic or formation brine and then flooded with crude oil to simulate the inflow of oil into the reservoir. When crude oil for wettability restoration is obtained, precautions should be taken to minimize alterations to the crude. The sample must be taken before any surfactants or other chemicals are added to treat the crude. It should be taken as long as possible after any well treatments to allow time for these chemicals to be flushed from the well. Finally, the crude should be sealed in air-tight containers as soon as possible to minimize oxidation and the loss of light ends.

The final step in wettability restoration is to age the core at the reservoir temperature for a sufficient time to establish adsorption equilibrium. The aging time required to re-establish reservoir wettability varies, depending on the crude, brine, and reservoir rock. Generally, we feel that core should be aged for 1,000 hours (40 days) at the reservoir temperature.¹²⁸ This aging period was chosen for two reasons: several experiments have shown that up to 1,000 hours is required to reach wetting equilibrium,^{64,65,115,189-191} and 1,000 hours is roughly the length of time required for the contact angle measured on a flat surface to approach its equilibrium value.^{7,26,34,192} In some cases, the restoration time can be significantly less than 1,000 hours. Mungan¹⁸⁰ was able to restore the wettability after aging for 6 days, while the wettability of the rock/oil/brine system used by Schmid⁵⁰ and Rühl *et al.*¹⁸⁸ was restored after only 3 days. Salathiel⁴⁷ was able to restore a mixed-wettability state to samples after 3 days. Cuiec *et al.*¹³⁰ describes two reservoirs in which the wettability was restored after only a few hours, with no further changes in the wettability for aging times as long as 1,000 hours.

There are two basic options to determine the aging time to restore wettability. We feel that it is most convenient to age all cores for 1,000 hours, which is roughly the maximum time that the experiments discussed previously required to achieve wetting equilibrium. While cores may

be aged for a period longer than the minimum necessary, this is not a serious drawback because the aging cores require minimal attention. Another possibility is to determine the minimum aging time by measuring the wettability of the core with the USBM or Amott methods at frequent intervals during the aging period. The aging is stopped when the wettability reaches its equilibrium value. Although this minimizes aging time, it is much less convenient because it is labor intensive and requires frequent disturbances to the plug.

The core is aged at either the reservoir pressure with live crude^{50,180,188,191} or ambient pressure with dead crude.^{115,128,190} When live crude oils and the reservoir pressure are used, the solubilities of the wettability-altering compounds should have their reservoir values. It is possible that the wettability will differ when dead crudes at ambient pressure are used. At the present time, however, it is not known whether the difference is important.

Fig. 1 shows the changes in the USBM wettability index as a core was restored.* A series of Berea plugs was saturated with brine and driven to IWS by centrifugation in crude oil. Each core was aged in dead crude for a different period of time, after which the USBM wettability was measured. As can be seen, the wettability changed from water-wet ($W=0.8$) to moderately oil-wet ($W=-0.3$) over a 40-day period. The plugs flushed with Soltrol® and Blandol® will be discussed later.

Lorenz *et al.*¹⁹⁰ and Cuiec⁶⁵ found that it is sometimes possible to speed up the approach to wetting equilibrium by saturating the core with oil alone. The approach to equilibrium is faster because the polar compounds no longer have to diffuse across a water layer to adsorb on the rock. This procedure should be avoided, however, because it can give inaccurate results. For example, consider the restoration of a core that originally had Salathiel's⁴⁷ mixed wettability, where the large pores are oil-wet and the small ones are water-wet. During the aging process, the small pores must contain connate water to prevent the deposition of an oil-wet film, leaving them water-wet. On the other hand, if a clean core is saturated only with oil, the entire core, including the small pores, will become uniformly oil-wet, which is the wrong wettability. An additional problem with saturating the core solely with oil is that the effects of brine chemistry are ignored. As discussed previously, the wettability of the core depends on the ionic composition and pH of the brine. Finally, Clementz^{104,120,121} showed that flowing crude oil through a dry core can cause the formation of very stable oil-wet, clay/organic complexes. The presence of an initial water film on the clay surfaces has been shown to reduce but not completely inhibit the adsorption of the wettability-altering materials.^{60,69,70} The effects of brine on wettability make it necessary to saturate the core with brine, then oil, during the wettability restoration process.

Experimental Conditions

Once a native- or restored-state core is obtained, core analyses can be performed. These tests can be run with either crude or refined oil at ambient or reservoir temperature and pressure. Because wettability effects are being ig-

nored, cleaned cores are generally run with refined oil (or even mercury or air) at room temperature and pressure. From the viewpoint of maintaining the wettability, the best laboratory tests should be run with native or restored cores at reservoir conditions with live crude oil and brine because this is the best simulation of reservoir conditions possible. Cores are generally more water-wet at reservoir conditions than they are at room temperature and pressure.^{62,180,192-195} The effects of the following experimental conditions on wettability will be discussed: (1) reservoir vs. room temperature, (2) live vs. dead crude at reservoir pressure, and (3) refined vs. crude oils.

Changing the temperature has two different effects, both of which tend to make the core more water-wet at higher temperatures. First, an increase in temperature tends to increase the solubility of wettability-altering compounds.¹⁹⁶ Some of these compounds will even desorb from the surface as the temperature increases. Second, the IFT and the contact angle measured through the water will decrease as the temperature increases. This effect has been noted in experiments with cleaned cores, mineral oil, and brine, where it was found that cores at higher temperatures were more water-wet even though there were no compounds that could adsorb and desorb.¹⁹⁷⁻²⁰⁰ For example, McCaffery²⁰¹ measured the water-advancing contact angle on quartz of n-tetradecane and brine. The angle was about 40° [0.7 rad] at 77°F [25°C], but decreased to about 15° [0.3 rad] as the temperature was raised to 300°F [150°C].

When live crude oils at the reservoir pressure and temperature are used, the solubilities of the wettability-altering compounds have their reservoir values. The use of dead crude at ambient or reservoir pressure may change the wettability because the properties of the crude are altered. Light ends are lost from the crude, while the heavy ends are less soluble, which may make the core more oil-wet. However, the effects of pressure are not known at present. The two reported experiments found that pressure is much less important than temperature.^{180,192} Hjelmeland and Larrondo¹⁹² found little difference in contact angles measured using stock-tank vs. live crude at the reservoir temperature (190°F [88°C]) and pressure (3,800 psi [26.2 MPa]). Mungan¹⁸⁰ measured a water-advancing contact angle of 87° [1.5 rad] using live reservoir crude and synthetic formation brine at reservoir temperature (138°F [59°C]) and pressure (1,200 psi [8.3 MPa]). The water-advancing contact angle was almost identical, 85° [1.48 rad], using degassed crude and brine at ambient pressure and reservoir temperature.

Because refined oils are much easier to work with than crude, it is a common laboratory practice to flush native- or restored-state cores with refined oil before testing. However, there is a possibility that this alters the wettability. Craig⁷ postulated that it would be possible, once the original wettability was restored, to use refined mineral oil in place of crude oil in laboratory tests without adversely affecting the wettability. Test times are short compared with the time it takes to achieve adsorption equilibrium and obtain native wettability (about 1,000 hours). Craig hypothesized that the desorption of wettability-influencing materials would require a correspondingly long period of time. If this is correct, the original wettability would be unchanged if laboratory tests using refined oil and brine were conducted quickly enough.

*Personal communication with D.J. Wendel, Petroleum Testing Services, Santa Fe Springs, CA, Nov. 1980.

The only experiment to test this hypothesis that we are aware of was conducted by Wendel.* He aged Big Muddy crude in Berea sandstone at IWS to develop his restored-state cores. The cores were flushed with one of two refined oils, Soltrol 170 or Blandol, to determine how they affected the wettability. The results are shown in Fig. 1. Blandol did not significantly affect the wettability, while Soltrol 170 changed the core from oil-wet to neutrally wet. The wettability alteration could be caused by either surface-active impurities in the Soltrol¹⁷⁵ or desorption of previously deposited oil-wetting crude compounds from the pore walls into the Soltrol. It is not known which explanation is correct. Wendel did not attempt to filter the refined oils through a chromatographic column to remove surface-active compounds. These contaminants are known to have a large effect on contact-angle measurements, which are extremely sensitive to small amounts of contaminants. Wettability measurements in core should be less sensitive, however, because the ratio of surface area to volume is much higher.

Conclusions

1. The wettability of a reservoir sample affects its capillary pressure, relative permeability, waterflood behavior, dispersion, and electrical properties. In addition, simulated tertiary recovery can be altered. The tertiary recovery processes affected by wettability include hot-water, surfactant, miscible, and caustic flooding.

2. Cleaned, strongly water-wet cores should be used only in such core analyses as porosity and air permeability, where the wettability is unimportant. In addition, they may be used in other tests when the reservoir is known to be strongly water-wet.

3. The wettability of originally water-wet mineral surfaces can be altered by the adsorption of polar compounds and/or the deposition of organic matter that was originally in the crude oil. Surfactants in the crude oil are generally believed to be polar compounds that contain oxygen, nitrogen, and/or sulfur. These compounds are most prevalent in the heavier fractions of crude oil, such as the resins and asphaltenes.

4. Wettability alteration is determined by the interaction of the oil constituents, the mineral surface, and the brine chemistry, including ionic composition and pH. In silica/oil/brine systems, trace amounts of multivalent metal cations can alter the wettability. The cations can reduce the solubility of crude oil surfactants and/or activate the adsorption of anionic surfactants onto the silica. Multivalent ions that have altered the wettability of silica/oil/brine systems include Ca^{+2} , Mg^{+2} , Cu^{+2} , Ni^{+2} , and Fe^{+3} .

5. Work on mineral flotation indicates that coal, graphite, sulfur, talc, the talc-like silicates, and many sulfides are probably naturally neutrally wet to oil-wet. Most other minerals—including quartz, carbonates, and sulfates—are strongly water-wet in their natural state.

6. Contact-angle measurements suggest that most carbonate reservoirs range from neutrally to oil-wet as a result of the adsorption of surfactants from the crude oil.

7. Very little work has been reported about the changes in wettability caused by drilling mud additives. Three different coring fluids have been recommended to obtain native-state core: (1) synthetic formation brine, (2) un-

oxidized lease crude oil, or (3) a water-based mud with a minimum of additives. Because of surfactants in the system, no commercially available oil-based or oil-emulsion muds are known that preserve the native wettability.

8. The wettability of a native-state core can be altered by loss of light ends and/or the deposition and oxidation of heavy ends. Two alternative packaging procedures can be used to minimize these effects. The first is to immerse the cores in deoxygenated formation or synthetic brine and place them in a glass-lined steel or plastic tube, which is then sealed against leakage and the entrance of oxygen. An alternative procedure is to wrap the cores at the well-site in polyethylene or polyvinylidene film and then in aluminum foil. The wrapped core is then coated with a thick layer of paraffin or a plastic sealer.

9. Because of the increased solubility of the wettability-altering compounds at the higher temperature and pressure, the crude-oil/brine/core system is usually more water-wet at reservoir conditions than at ambient conditions. In addition, the contact angle measured through the water will generally decrease as the temperature is increased, and the system will become more water-wet, even if no surfactants are present.

10. Extraction with toluene can alter the wettability of some native-state cores, causing some initially neutrally wet or mildly oil-wet cores to become strongly water-wet. Measurements on native-state cores should be made before toluene extraction.

11. During the attempted restoration of a cleaned core to its original wettability, the core should be saturated with brine, oilflooded, and then aged at the reservoir conditions for 1,000 hours. This will enable a mixed-wettability condition to be restored, if this was the original wettability. In addition, it will allow the brine chemistry to influence the restored wettability. An alternative procedure, which completely saturates the core with crude oil, should be avoided.

12. The three commonly used methods for artificially controlling wettability during laboratory experiments are (1) treatment of the core with chemicals, generally organochlorosilane solutions for sandstone cores and naphthenic acids for carbonate cores; (2) using sintered teflon cores with pure fluids; and (3) adding surfactants to the fluids. To obtain a uniformly wetted core, a sintered teflon core with pure fluids is preferred because its wettability is more constant and reproducible than the wettability of cores treated with organochlorosilanes, naphthenic acids, or surfactants. However, these treatments have advantages when heterogeneous wettability or wettability alteration is studied.

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SI Metric Conversion Factors

$$\begin{array}{lll} \text{degrees} & \times 1.745\ 329 & \text{E-02} = \text{rad} \\ ^\circ\text{F} & (^\circ\text{F}-32)/1.8 & = ^\circ\text{C} \end{array}$$

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Wettability Literature Survey— Part 2: Wettability Measurement

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SPE 13933

Summary. Many methods have been used to measure wettability. This paper describes the three quantitative methods in use today: contact angle, Amott method, and the U.S. Bureau of Mines (USBM) method. The advantages and limitations of all the qualitative methods—imbibition, microscope examination, flotation, glass slide, relative permeability curves, capillary pressure curves, capillarimetric method, displacement capillary pressure, permeability/saturation relationships, and reservoir logs—are covered. Nuclear magnetic resonance (NMR) and dye adsorption, two methods for measuring fractional wettability, are also discussed. Finally, a method is proposed to determine whether a core has mixed wettability.

Introduction

This paper is the second in a series of literature surveys covering the effects of wettability on core analysis.¹⁻³ Changes in the wettability of cores have been shown to affect electrical properties, capillary pressure, waterflood behavior, relative permeability, dispersion, and simulated EOR. For core analysis to predict the behavior of the reservoir, the wettability of the core must be the same as the wettability of the undisturbed reservoir rock.

When a drop of water is placed on a surface immersed in oil, a contact angle is formed that ranges from 0 to 180° [0 to 3.14 rad]. A typical oil/water/solid system is shown in Fig. 1, where the surface energies in the system are related by Young's equation,⁴

$$\sigma_{ow} \cos \theta = \sigma_{os} - \sigma_{ws}, \quad (1)$$

where

- σ_{ow} = interfacial energy [interfacial tension (IFT)] between the oil and water,
- σ_{os} = interfacial energy between the oil and solid,
- σ_{ws} = interfacial energy between the water and solid, and
- θ = contact angle, the angle of the water/oil/solid contact line.

By convention, the contact angle, θ , is measured through the water. The interfacial energy σ_{ow} is equal to σ , the IFT.

As shown in Fig. 1, when the contact angle is less than 90° [1.6 rad], the surface is preferentially water-wet, and when it is greater than 90° [1.6 rad], the surface is preferentially oil-wet. For almost all pure fluids and clean rock or polished crystal surfaces, σ_{os} and σ_{ws} have values such that $\theta = 0^\circ$ [0 rad]. When compounds such as crude-oil components are adsorbed on rock surfaces, these interfacial energies are changed unequally. This changes θ and hence the wettability. The farther θ is from 90° [1.6

rad], the greater the wetting preference for one fluid over another. If θ is exactly 90° [1.6 rad], neither fluid preferentially wets the solid. As shown in Table 1, when θ is between 0 and 60 to 75° [0 and 1 to 1.3 rad], the system is defined as water-wet. When θ is between 180 and 105 to 120° [3.1 and 1.8 to 2.1 rad], the system is defined as oil-wet. In the middle range of contact angles, a system is neutrally or intermediately wet. The contact angle that is chosen as the cutoff varies from paper to paper.

The term $\sigma_{os} - \sigma_{ws}$ is sometimes called the adhesion tension, σ_A :⁵

$$\sigma_A = \sigma_{os} - \sigma_{ws} = \sigma_{ow} \cos \theta. \quad (2)$$

The adhesion tension is positive when the system is water-wet, negative when the system is oil-wet, and near zero when the system is neutrally wet.

Methods of Wettability Measurement

Many different methods have been proposed for measuring the wettability of a system.⁶⁻¹⁶ They include quantitative methods—contact angles, imbibition and forced displacement (Amott), and USBM wettability method—and qualitative methods—imbibition rates, microscope examination, flotation, glass slide method, relative permeability curves, permeability/saturation relationships, capillary pressure curves, capillarimetric method, displacement capillary pressure, reservoir logs, nuclear magnetic resonance, and dye adsorption.

Although no single accepted method exists, three quantitative methods generally are used: (1) contact-angle measurement, (2) the Amott⁶ method (imbibition and forced displacement), and (3) the USBM method.^{9,17,18} The contact angle measures the wettability of a specific surface, while the Amott and USBM methods measure the average wettability of a core. A comparison of the wettability criteria for the three methods is shown in Table 1. The remaining tests in the list are qualitative, each with somewhat different criteria to determine the degree of water or oil wetness. Unfortunately, this leads to am-

biguities when experiments in the literature are compared. Many of the wettability measurements are also imprecise, particularly near neutral wettability. One method may show that a core is mildly oil-wet, while another shows that the core is mildly water-wet. In this paper, the different methods of wettability measurement are described, beginning with the quantitative methods. The more qualitative methods are then described, followed by the methods for measuring the wettability of fractional and mixed-wettability cores.

Quantitative Wettability Measurements

Contact Angle. The contact angle is the best wettability measurement method when pure fluids and artificial cores are used because there is no possibility of surfactants or other compounds altering the wettability. The method is also used to determine whether a crude oil can alter wettability and to examine the effects of temperature, pressure, and brine chemistry on wettability. However, as discussed in more detail later, some difficulties are involved in applying contact-angle measurements to reservoir cores. Many methods of contact-angle measurement have been used. They include the tilting plate method, sessile drops or bubbles, vertical rod method, tensiometric method, cylinder method, and capillary rise method.

Descriptions of these methods can be found in Adamson,⁴ Johnson and Dettre,¹⁹ Good,²⁰ Neumann and Good,²¹ and Popiel.²² Most of these methods are not generally used in the petroleum industry, however, because they are better suited for pure fluids with no adsorption or desorption of surfactants. Because of the surface-active agents in crude, a significant length of time is needed for a contact angle to reach equilibrium.

The methods that are generally used in the petroleum industry are the sessile drop method^{21,23-25} and a modified form of the sessile drop method described by Leach *et al.*²⁶ and Treiber *et al.*²⁷ In both methods, the mineral crystal to be tested is mounted in a test cell composed entirely of inert materials to prevent contamination. The sessile drop method uses a single flat, polished mineral crystal (see Fig. 1). The modified sessile drop method uses two flat, polished mineral crystals that are mounted parallel to each other on adjustable posts, as shown in Fig. 2a. Because sandstones are often composed primarily of quartz and limestones of calcite, quartz or calcite crystals are used to simulate the pore surfaces of the reservoir rock. Obviously, the wettability of clays in the reservoir cannot be examined with this method.

The first step in measuring contact angle is to clean the apparatus thoroughly, because even trace amounts of contaminants can alter the contact angle. Then the cell con-

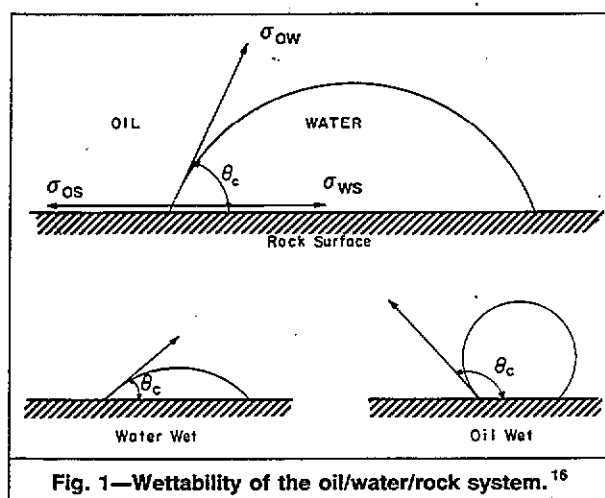


Fig. 1—Wettability of the oil/water/rock system.¹⁶

taining the mineral crystals is filled with brine. Deoxygenated synthetic formation brine is used to prevent the introduction of foreign metal ions, which in concentrations of only a few parts per million can alter the wettability.^{1,27} For the modified sessile drop method, an oil drop is placed between the two crystals so that it contacts a large area of each crystal. After the oil/crystal interface has aged for a few days, the two crystals are displaced parallel to each other. As shown in Fig. 2b, this shifts the oil drop and allows brine to move over a portion of the surface previously covered with oil. The contact angles measured in this fashion are called "water-advancing" contact angles. A nonequilibrium angle is observed immediately after the drop is moved. This angle decreases for a day or two until a constant value is obtained for that age of the oil/solid interface. The oil/mineral surface is then aged further, the water is advanced again, and a new value is obtained.

The procedures are similar in the sessile drop method. A drop of crude oil is formed at the end of a fine capillary tube and brought into contact with the flat mineral surface (see Fig. 1). The droplet is allowed to age on the surface. The water-advancing and water-receding contact angles are measured by using the capillary tube to expand and contract the volume of the crude-oil drop.^{23,24}

When the crude oil contains natural surface-active substances, the water-advancing contact angle increases as the oil/crystal interface ages, approaching a limiting value as adsorption equilibrium is reached. To achieve this limiting value may require hundreds or even thousands of hours of interface-aging time. Fig. 3²⁷ gives examples of the change in the water-advancing contact angle as the oil/solid interface ages. This demonstrates that early meas-

TABLE 1—APPROXIMATE RELATIONSHIP BETWEEN WETTABILITY, CONTACT ANGLE, AND THE USBM AND AMOTT WETTABILITY INDEXES

	Water-Wet	Neutrally Wet	Oil-Wet
Contact angle			
Minimum	0°	60 to 75°	105 to 120°
Maximum	60 to 75°	105 to 120°	180°
USBM wettability index	W near 1	W near 0	W near -1
Amott wettability index			
Displacement-by-water ratio	Positive	Zero	Zero
Displacement-by-oil ratio	Zero	Zero	Positive
Amott-Harvey wettability index	0.3 ≤ I ≤ 1.0	-0.3 < I < 0.3	-1.0 ≤ I ≤ -0.3

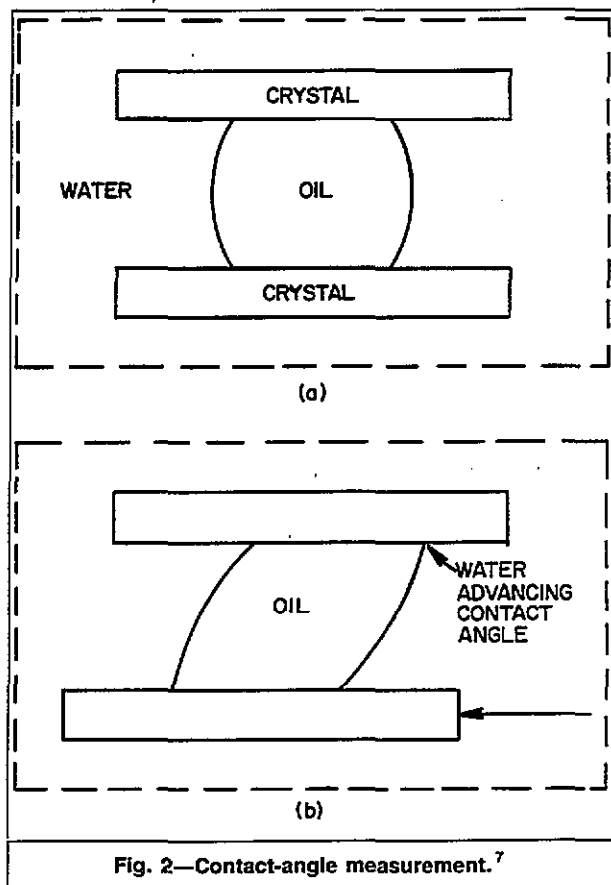


Fig. 2—Contact-angle measurement.⁷

urements can show that the system is water-wet even though it is actually oil-wet at equilibrium. Because it contains no surfactants, the contact angle for pure decane (Curve A) did not change from zero as the interface was aged.

One problem in contact-angle measurements is hysteresis, because it is generally found experimentally that a liquid drop on a surface can have many different stable contact angles. The contact angles reported in the literature are either the water-advancing or water-receding contact angle because these two angles are the most reproducible. The water-advancing angle can also be thought of as the oil-receding one. The advancing angle, θ_{adv} , is measured by pulling the periphery of a drop over a surface, while the receding contact angle, θ_{rec} , is measured by pushing it back. The difference, $\theta_{adv} - \theta_{rec}$, is the contact-angle hysteresis and can be greater than 60° [1 rad].¹⁹

Johnson and Dettre¹⁹ and Adamson⁴ state that there appear to be three causes of contact-angle hysteresis: (1) surface roughness, (2) surface heterogeneity, and (3) surface immobility on a macromolecular scale. To see how surface roughness can cause hysteresis, consider a horizontal but rough plate. Because the rough surface contains peaks and valleys, a liquid drop will generally be attached to a surface that is not horizontal. The macroscopically observed contact angle will not be the same as the true contact angle on a microscopic scale. The roughness of the surface will allow a large number of metastable states of the drop to exist with different contact angles. The surface roughness will generally diminish the apparent contact angle for water-wet rock and increase it for oil-wet rock.^{19,22}

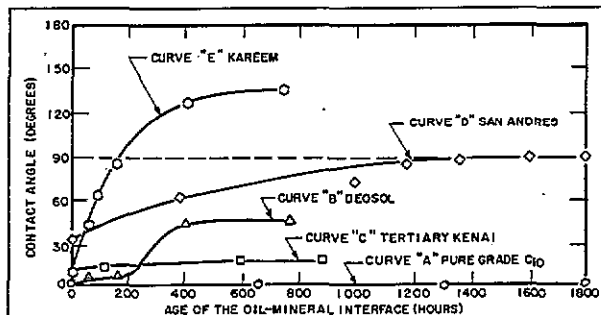


Fig. 3—Approach to equilibrium contact angle.²⁷

Hysteresis resulting from surface heterogeneity can be caused by either heterogeneity in the rock surface composition or differential adsorption of wettability-altering compounds. This problem is generally avoided by measuring the angle on a single crystal and by rigorously cleaning the entire apparatus before measurement. Finally, surface immobility can cause hysteresis by preventing the fluid motion necessary for the contact angle to reach its equilibrium value. For example, slow adsorption of a surfactant from the solid/liquid interface into the bulk liquid can cause hysteresis. Some crude oils can even form a solid film at the oil/water interface.²⁸⁻³⁰ These films are particularly likely to form if the crude has been exposed to oxygen, but have even been found in some anaerobic crudes.

Even though it is possible, with great care, to get exact and reproducible contact-angle measurements, the question of how representative these results are of the wettability of reservoir core arises. The contact angle cannot take into account the roughness, heterogeneity, and complex geometry of reservoir rock. First, consider the problems caused by roughness. Morrow³¹ has pointed out that roughness and pore geometry will influence the oil/water/solid contact line and can change the apparent contact angle. On a smooth surface, the contact angle is fixed. On the sharp edges found in reservoir rock, however, this condition is relaxed, and there is a wide range of possible contact angles.^{31,32} Morrow postulates that most of the oil/water/rock contact lines will be located at the sharp edges because, at these edges, the contact angle can change without moving the position of the contact line.

A second problem with applying contact-angle measurements to reservoir rocks is that the contact angle cannot take into account the heterogeneity of the rock surface. Contact angles are measured on a single mineral crystal, while a core contains many different constituents. As discussed previously, surfactants in the crude can affect the wettability of the sands and clays differently, causing localized heterogeneous wettability.

A third limitation is that no information can be gained about the presence or absence of permanently attached organic coatings on reservoir rocks.³³ These films can be detected only by making other wettability measurements. This is particularly important when working with restored-state cores.^{34,35} Before the original wettability can be restored, all the adsorbed materials must be removed, which will generally leave the core in a strongly water-wet state. The only way to determine whether the cleaning process has been successful is to measure the wet-

tability of the cleaned core. If it is not strongly water-wet, additional cleaning is necessary.

Amott Method. The Amott method^{6,8,36} combines imbibition and forced displacement to measure the average wettability of a core. Both reservoir core and fluids can be used in the test. The Amott method is based on the fact that the wetting fluid will generally imbibe spontaneously into the core, displacing the nonwetting one. The ratio of spontaneous imbibition to forced imbibition is used to reduce the influence of other factors, such as relative permeability, viscosity, and the initial saturation of the rock.

Core is prepared by centrifuging under brine until the residual oil saturation (ROS) is reached. The Amott wettability measurement then consists of the following four steps: (1) immerse the core in oil, and measure the volume of water displaced by the spontaneous (free) imbibition of oil after 20 hours; (2) centrifuge the core in oil until the irreducible water saturation (IWS) is reached, and measure the total amount of water displaced, including the volume displaced by spontaneous imbibition; (3) immerse the core in brine, and measure the volume of oil spontaneously displaced by imbibition of water after 20 hours; and (4) centrifuge the core in oil until ROS is reached, and measure the total amount of oil displaced. Note that the core may be driven to IWS and ROS by flow rather than with a centrifuge. This is especially necessary for unconsolidated material that cannot be centrifuged.

The test results are expressed by (1) the "displacement-by-oil ratio"—the ratio of the water volume displaced by spontaneous oil imbibition alone, V_{wsp} , to the total displaced by oil imbibition and centrifugal (forced) displacement, V_{wt} ,

$$\delta_o = \frac{V_{wsp}}{V_{wt}}, \dots\dots\dots (3a)$$

and (2) the "displacement-by-water ratio"—the ratio of the oil volume displaced by spontaneous water imbibition, V_{osp} , to the total oil volume displaced by imbibition and centrifugal (forced) displacement, V_{ot} :

$$\delta_w = \frac{V_{osp}}{V_{ot}}, \dots\dots\dots (3b)$$

As shown in Table 1, preferentially water-wet cores have a positive displacement-by-water ratio and a zero value for the displacement-by-oil ratio. The displacement-by-water ratio approaches 1 as the water wetness increases. Similarly, oil-wet cores have a positive displacement-by-oil ratio and a zero displacement-by-water ratio. Both ratios are zero for neutrally wet cores.

Amott chose an arbitrary time period of 20 hours for the spontaneous oil and water imbibition steps in his method. If possible, we recommend instead that the cores be allowed to imbibe until either imbibition is complete or a time limit of 1 to 2 weeks is reached. Imbibition can take from several hours to more than 2 months to complete.³⁴ If the imbibition is stopped after a short period of time, then the measured spontaneous imbibition volume will be lower than the equilibrium value for low-

permeability samples, causing an underestimation of δ_o or δ_w .^{8,36} The measured displacement ratios will underestimate the water- or oil-wetness of the rock. Of course, it is necessary to choose some upper time limit to finish the measurement in a reasonable length of time. If the core is still imbibing when the time limit is reached, however, then the measured spontaneous imbibition volume will underestimate the reservoir wettability, and the Amott ratios should be interpreted with caution.^{8,36}

A number of researchers^{37,38} used a modification of the Amott wettability test called the "Amott-Harvey relative displacement index." This procedure has an additional step in the core preparation before the test is run: the core is centrifuged first under brine and then under crude to reduce the plug to IWS. The displacement-by-water and displacement-by-oil ratios are then calculated by the Amott method. The Amott-Harvey relative displacement index is the displacement-by-water ratio minus the displacement-by-oil ratio:

$$I = \delta_w - \delta_o = \frac{V_{osp}}{V_{ot}} - \frac{V_{wsp}}{V_{wt}} \dots\dots\dots (4)$$

This combines the two ratios into a single wettability index that varies from +1 for complete water wetness to -1 for complete oil wetness. Cuiec³⁹ states that the system is water-wet when $+0.3 \leq I \leq 1$, intermediate wet when $-0.3 < I < 0.3$, and oil-wet when $-1 \leq I \leq -0.3$.

The Amott test measures the total volume of spontaneous and forced oil and water imbibition. Morrow *et al.*⁴⁰ developed a modified form of the Amott test, which also measures the imbibition rates during the spontaneous imbibition measurements. In this test, the core is suspended in oil or water from an electronic balance by a small monofilament line. Weight change is monitored as a function of time as the spontaneous imbibition occurs. The wettability of the core is then determined from both the Amott wettability index and the spontaneous imbibition rates. This test may offer some advantages over the standard Amott test because it is based on additional data.

The main problem with the Amott wettability test and its modifications is that they are insensitive near neutral wettability. The test measures the ease with which the wetting fluid can spontaneously displace the nonwetting one. However, neither fluid will spontaneously imbibe and displace the other when the contact angle varies from roughly 60 to 120° [1 to 2.1 rad].^{3,41-45} In addition, the limiting contact angle above which spontaneous imbibition will not occur depends on the initial saturation of the core. McCaffery⁴¹ and Morrow and McCaffery⁴⁵ examined the spontaneous imbibition of pure fluids with a known contact angle into a synthetic teflon core that initially contained air. In the experiments, n-dodecane ($\theta=42^\circ$ [0.7 rad]) would always spontaneously imbibe into the core, while α -bromonaphthalene ($\theta=73^\circ$ [1.3 rad]) would never spontaneously imbibe. Dioctyl ether ($\theta=49^\circ$ [0.9 rad]) would not imbibe into a dry core but would imbibe into a core with an initial dioctyl ether saturation of 30%. The Amott method would classify the teflon core with n-dodecane as mildly water-wet, while α -bromonaphthalene would be neutrally wet. The core with dioctyl ether ($\theta=49^\circ$ [0.9 rad]) would be classified as water-wet if it already contained some fluid or as neutrally wet if the core was initially dry.

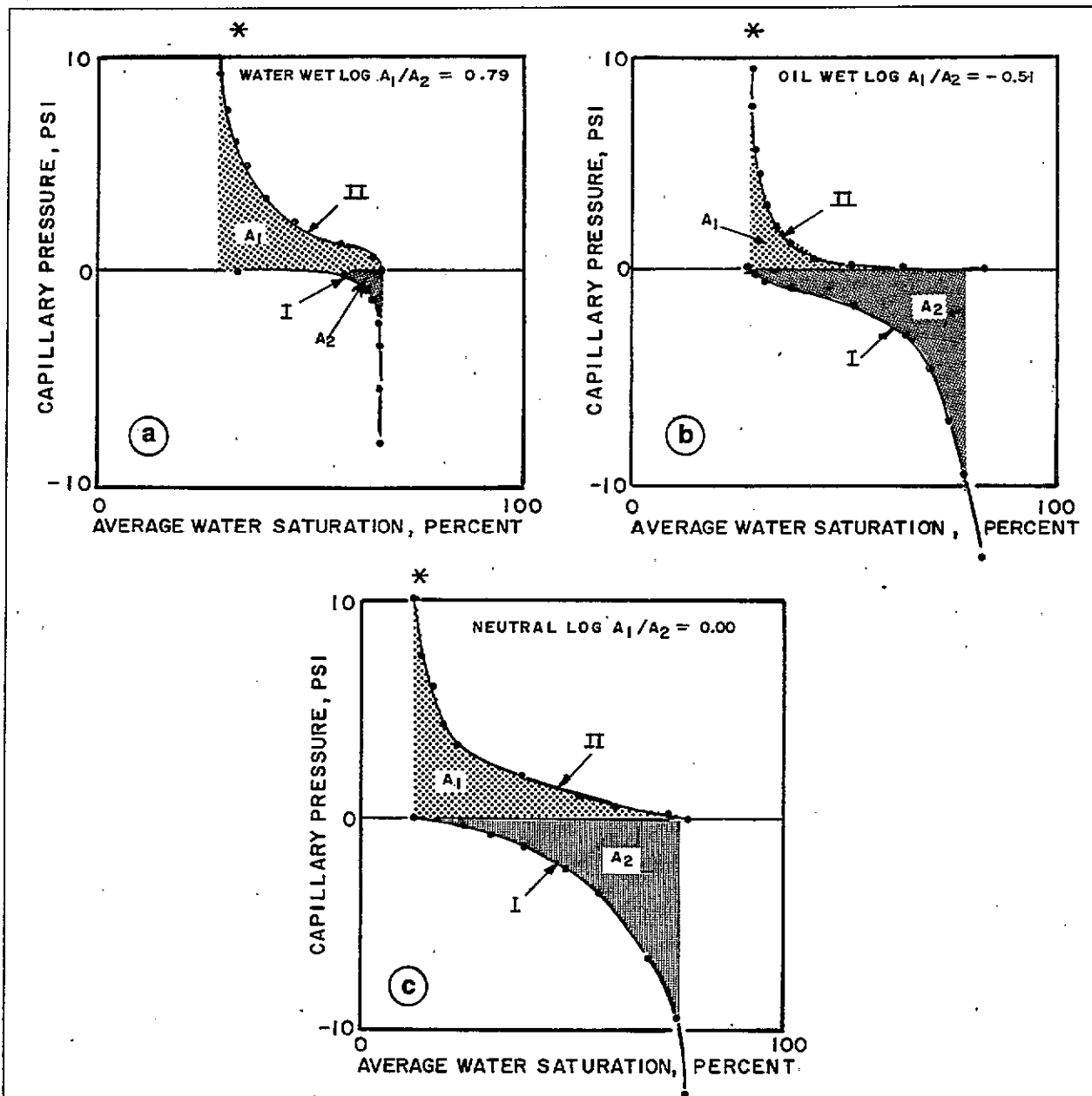


Fig. 4—USBM wettability measurement⁹: (I—brine drive, II—oil drive) (a) untreated core, (b) core treated with organochlorosilanes, (c) core pretreated with oil for 324 hours at 140°F; brine contains 1,000 ppm sodium tripolyphosphate.

USBM Wettability Index. The third quantitative test that is used to measure the wettability is the USBM test developed by Donaldson *et al.*^{9,17,18} The USBM test also measures the average wettability of the core. The test is relatively rapid, requiring a few days to test four to eight plugs. A major advantage it has over the Amott wettability test is its sensitivity near neutral wettability. A minor disadvantage is that the USBM wettability index can only be measured on plug-size samples because the samples must be spun in a centrifuge. The USBM test compares the work necessary for one fluid to displace the other. Because of the favorable free-energy change, the work required for the wetting fluid to displace the nonwetting fluid from the core is less than the work required for the opposite displacement. It has been shown that the required work is proportional to the area under the capillary pressure curve.^{31,46} In other words, when a core is water-

wet, the area under the brine-drive capillary pressure curve (when the water displaces the oil) is smaller than the area under the capillary pressure curve for the reverse displacement. In fact, if the water-wetting is strong enough, most of the water will spontaneously imbibe into the core, and the area under the brine-drive curve will be very small.

Before the test is run, plugs are prepared by centrifugation under oil at high speed to drive them to IWS. This point is denoted by the asterisks (*) in Figs. 4a through 4c, which represent wettability test results in cores with three different surface treatments. During the USBM measurement, a modified version of the procedure described by Hassler and Brunner⁴⁷ and Slobod *et al.*⁴⁸ is used to calculate the centrifugal capillary pressures. (The USBM method uses the average saturations in the core.¹⁷ In contrast, the centrifugal capillary pressure curve is

based on the saturation at the face of the core, which is calculated from the average saturation by the method found in Ref. 47.) In the first step of the measurement, cores are placed in brine and centrifuged at incrementally increasing speeds until a capillary pressure of -10 psi [-70 kPa] is reached. This step is known as the brine drive because brine displaces oil from the core. At each incremental capillary pressure, the average saturation of the plug is calculated from the volume of expelled oil. Curve I (Figs. 4a through 4c) is a plot of capillary pressure vs. the average saturation for the brine drive.

In the second step, the core is placed in oil and centrifuged. During this oil-drive step, oil displaces brine from the core. As in the first step, the capillary pressures and average saturations are measured until a capillary pressure of 10 psi [70 kPa] is reached. In each case, the curves are linearly extrapolated or truncated if the last pressure is not exactly 10 psi [70 kPa]. The results of the oil drive are plotted as Curve II in Figs. 4a through 4c.

The USBM method uses the ratio of areas under the two capillary pressure curves to calculate a wettability index according to Eq. 5.

$$W = \log(A_1/A_2), \dots\dots\dots (5)$$

where A_1 and A_2 are the areas under the oil- and brine-drive curves, respectively. As shown in Table 1, when W is greater than zero, the core is water-wet, and when W is less than zero, the core is oil-wet. A wettability index near zero means that the core is neutrally wet. The larger the absolute value of W , the greater the wetting preference.

Examples of water-wet, oil-wet, and neutrally wet cores are shown in Figs. 4a through 4c for an initially water-wet outcrop Torpedo sandstone core. Fig. 4a shows the USBM wettability index of the untreated water-wet core. The area under the oil-drive curve is much larger than the area under the water-drive curve, yielding a wettability index of 0.79. In Fig. 4b, the core was treated with an organosilane compound, which rendered it oil-wet. The area under the oil-drive curve is now much smaller than the area under the water-drive curve because oil is the wetting fluid, yielding a wettability index of -0.51. In Fig. 4c, the core was aged with crude, and the brine was treated with sodium tripolyphosphate. The core is now neutrally wet, and both of the areas are equal, making the USBM wettability index zero.

A major advantage of the USBM wettability test over the Amott test is its sensitivity near neutral wettability. On the other hand, the USBM test cannot determine whether a system has fractional or mixed wettability, while the Amott test is sometimes sensitive. In some fractional- or mixed-wet systems, both water and oil will imbibe freely.⁴⁹⁻⁵¹ The Amott method will have positive displacement-by-water and displacement-by-oil ratios, indicating that the system is nonuniformly wetted.

Combined Amott/USBM Method. Sharma and Wunderlich⁵¹ have recently developed a modification of the USBM method that allows the calculation of both the Amott and USBM wettability indices. The procedure, shown in Fig. 5, has five steps: (1) initial oil drive, (2) spontaneous (free) imbibition of brine, (3) brine drive, (4) spontaneous (free) imbibition of oil, and (5) oil drive.

The areas under the brine- and oil-drive curves are used to calculate the USBM index, while the Amott index uses the volumes of free and total water and oil displacements.

During the initial oil-drive step (Curve 1), the plugs are driven to IWS. Next, the cores are immersed in water, and the volume of water that imbibes freely is measured (Curve 2). During the brine-drive step (Curve 3), the average saturation of the plug is determined from the amount of expelled oil at each incremental capillary pressure. These data are used to calculate the area under the brine-drive curve, A_2 , for the USBM method. At the end of the brine-drive step, the plug is left at ROS. The Amott displacement-by-water ratio, δ_w , is the ratio of the oil volume displaced by free brine imbibition to the total volume displaced by free imbibition and centrifugal displacement (Eq. 3a).

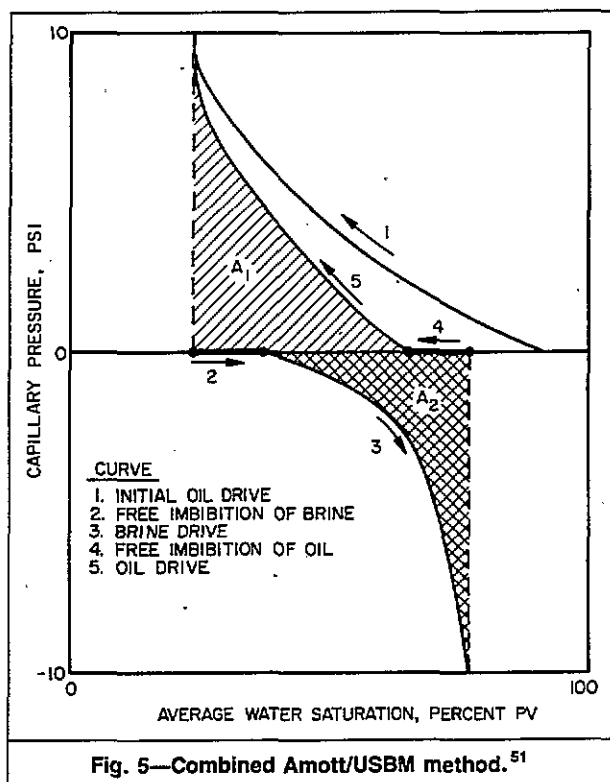
In the fourth step (Curve 4), the plug is immersed in oil, and the volume of oil that imbibes spontaneously is measured. The final step is the oil drive (Curve 5), where the capillary pressures and average saturations are used to calculate A_1 for the USBM method. Eq. 5 is then used to calculate the USBM wettability index. At the end of the oil drive, the plug is left at IWS. The Amott displacement-by-oil ratio, δ_o , is the ratio of the free oil imbibition to the total volume displaced by free imbibition and centrifugal displacement (Eq. 3b).

There are two advantages of the combined USBM/Amott method over the standard USBM method⁵¹: the resolution of the USBM method is improved by accounting for the saturation changes that occur at zero capillary pressure, and the Amott index is also calculated. As discussed earlier, the Amott method will sometimes indicate that a system is nonuniformly wetted.

Qualitative Wettability Measurements

Imbibition Method. The most commonly used qualitative wettability measurement is the imbibition method,⁵²⁻⁵⁷ because it gives a quick but rough idea of the wettability without requiring any complicated equipment. The original imbibition apparatus tested the wettability at room temperature and pressure.⁵²

More recently, Kyte *et al.*⁵⁷ described a modification of the apparatus that allows wettability to be measured at reservoir conditions. In an imbibition test, a core at IWS is first submerged in brine underneath a graduated cylinder, and the rate and amount of oil displaced by brine imbibition are measured. The core is strongly water-wet if large volumes of brine are rapidly imbibed, while lower rates and smaller volumes imply a more weakly water-wet core. If no water is imbibed, the core is either oil-wet or neutrally wet. Non-water-wet cores are then driven to ROS and submerged in oil. The imbibition apparatus is inverted, with the graduated cylinder below the core to measure the rate and volume of water displaced by oil imbibition. If the core imbibes oil, it is oil-wet. The strength of oil-wetness is indicated by the rate and volume of oil imbibition. If neither oil nor water is imbibed, the core is neutrally wet. Finally, some cores will imbibe both water and oil.⁴⁹⁻⁵¹ These cores have either fractional or mixed wettability. One problem with the imbibition method is that, in addition to wettability, imbibition rates also depend on relative permeability, viscosity, IFT, pore structure, and the initial saturation of the core.^{3,10} Frequently, this dependence on other variables is reduced by



comparison of the measured imbibition rate with a reference rate measured when the core is strongly water-wet. To do this, the core is cleaned by heating at 750°F [400°C] for 24 hours to oxidize all of the organic material, leaving the core strongly water-wet. The core is then resaturated to its original oil saturation with a refined white oil having the same viscosity as the crude oil, and the reference imbibition rate is measured. Denekas *et al.*⁵³ reported wettability changes in terms of the "relative rate" of imbibition:

$$R = \frac{\dot{m}}{\dot{m}_r}, \dots \dots \dots (6)$$

where

R = relative rate of imbibition,

\dot{m} = initial imbibition rate of the core just after it is submerged (cm^3/s), and

\dot{m}_r = initial imbibition rate of the cleaned, strongly water-wet core (cm^3/s).

If the core is water-wet, \dot{m} is the initial water imbibition rate. If the core is oil-wet, \dot{m} is the initial oil imbibition rate, and the relative imbibition rate, R , is reported as a negative number. Note, however, that while the use of a reference rate reduces the effect of other variables, the imbibition method still suffers from the same problem as the Amott method—insensitivity near neutral wettability.

Bobek *et al.*⁵² also suggested an imbibition test for unconsolidated cores. In this test, a thin layer of sand is spread on a microscope slide, after which the oil saturation is increased by addition of a refined mineral oil. Droplets of water are then placed on the surface of the sand, and the movement of the fluid is observed by micro-

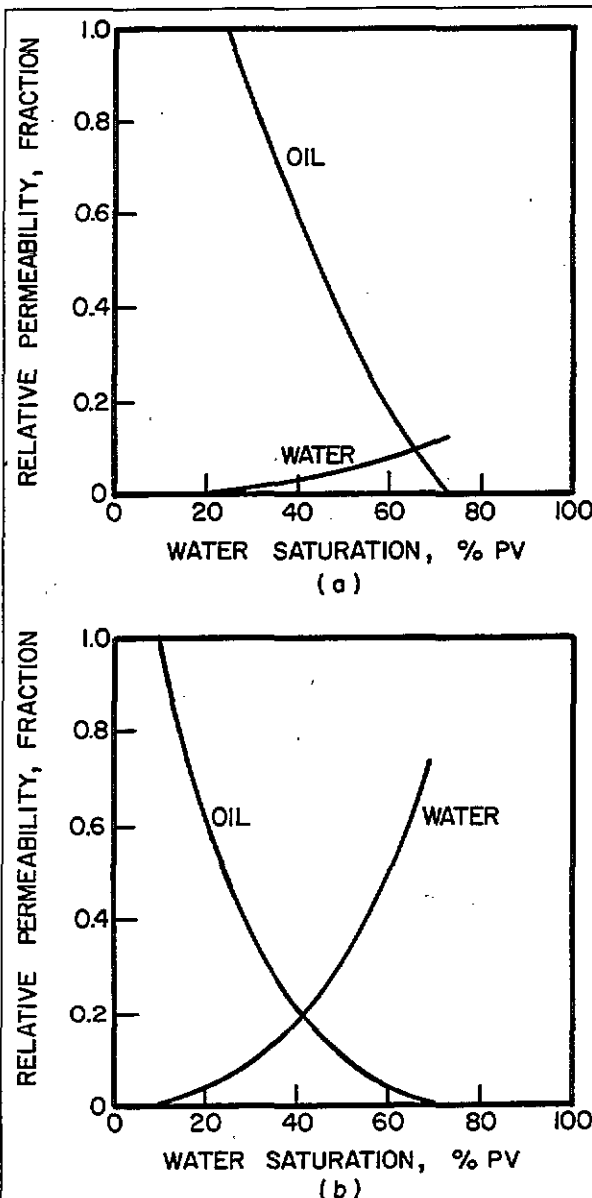


Fig. 6—Typical water/oil relative permeability curves based on the effective permeability to oil at the reservoir connate water saturation; (a) strongly water-wet rock, (b) strongly oil-wet rock.⁷

scope. If the sample is water-wet, the water will move readily into the sand, displacing oil from the surface of the sand grains. In addition, the oil will form spherical droplets, indicating that it is the nonwetting phase. A similar procedure is used to test for oil wettability. This test is similar to the microscope examination method.

Microscope Examination. Microscope examination is sometimes used in laboratory flow visualization studies. The wettability is determined from a description of the flow on a single pore level in an idealized porous medium during waterflooding.^{58,59} This description includes the structure of the residual oil and the changes in the location of the oil and water that occur during waterflooding. If the system is strongly water-wet, the water surrounds the grains as a thin film. The large pools of residual oil rest on a water film, while the smaller drops

of residual oil form spherical drops in the center of the pores. If the system is intermediately wet, both oil and water will be found in contact with the rock surfaces, and both can be found in the small pores. Finally, if the system is oil-wet, the roles of the oil and water are reversed. The oil forms a film around the grain surfaces and is found in the small pores, while the water rests on an oil film or forms small spheres.

The method of qualitatively determining the wettability by microscope examination is particularly important in the study of wettability reversals.^{58,60-64} One of the proposed mechanisms for EOR that occurs during alkaline waterflooding.⁵⁸ In these experiments, a chemical that changes the wettability is injected into the porous medium during a waterflood, causing a zone of wettability reversal to propagate through the core. A microscope is used to follow wettability changes and to determine whether EOR will occur by this mechanism.

Flotation Methods. Flotation methods are fast but work only for strongly wetted systems. In the simplest method, water, oil, and sand are placed in a glass bottle. The bottle is shaken, and the experimenter observes the fate of the sand grains.⁶⁵⁻⁶⁸ This method is recommended by API for determining the effects of surfactants on wettability.⁶⁵ If the system is strongly water-wet, clean sand grains will settle to the bottom of the bottle. Sand grains placed in the oil will aggregate and form small clumps of grains surrounded by a thin layer of water. If the system is oil-wet, some of the grains can be suspended at the oil/water interface. Oil-wet sand grains in the water will clump together, forming small oil globules coated with sand. This flotation system is qualitative and works only for strongly wetted systems.

Several experimenters^{69,70} have used more elaborate flotation tests developed in the mining industry that were based on liquid/liquid extraction.^{22,71} In these tests, particles are initially suspended in water. A second fluid, either oil or air, is bubbled from below. The particles that are water-wet remain in the water, while the hydrophobic, oil-wet particles adhere to the oil (air) and rise to the surface. The fraction of particles in each phase can then be measured. Clementz⁷⁰ used the flotation method to measure the wettability of small clay particles, which cannot be conveniently measured in any other way. Untreated, strongly water-wet particles would not float. After exposure to crude, the clay particles floated, demonstrating that their wettability had been altered.

Flotation tests based on liquid/liquid extraction appear to divide particles into two categories: strongly water-wet, and mildly water-wet to strongly oil-wet.^{72,73} Besides the wettability, flotation of a particle also depends on particle size, particle density, and IFT. A small particle with low density and high IFT might float if the contact angle was greater than about 30° [0.5 rad]. On the other hand, the minimum contact angle for flotation of a large, dense particle could be 90° [1.6 rad].^{72,73}

Glass Slide Method. Another early qualitative wettability measurement technique is the glass slide method,^{30,67} which assumes that a glass surface is representative of the reservoir rock. A clean, dry, glass microscope slide is suspended in a layer of crude oil floating on water in a transparent container and aged. The glass slide is then

lowered into the water. If the slide is water-wet, the water quickly displaces the oil on the slide. On the other hand, if the slide is oil-wet, a stable oil-wet film is formed, and the oil is very slowly displaced. Reisberg and Doscher³⁰ aged slides in crude oil and found that it took up to 30 days for the final wettability to be reached. Cooke *et al.*⁵⁸ used a simple variation of the glass slide method as a quick, qualitative test to screen different acidic-oil/alkaline-water combinations for use in alkaline waterflooding experiments. They placed oil and water without mixing in a glass vial and waited to see whether a stable oil-wet film formed on the vial. This was determined by tilting the vial and seeing how the water and oil behaved on the previously oil-covered surface.

Relative Permeability Methods. A number of qualitative methods are based on the effects of wettability on relative permeability. However, they are all suitable only for discriminating between strongly water-wet and strongly oil-wet cores. A smaller change in wettability—e.g., between strongly and moderately water-wet—may not be noticed by these methods. One method developed by Ehrlich and Wygal⁷⁴ is based on the rules of thumb given by Craig⁷ to differentiate between strongly water-wet and strongly oil-wet cores. Craig's^{16,52,75} rules of thumb are as follows.

1. Connate water saturations are usually greater than 20 to 25% PV in a water-wet rock, but less than 10% PV in an oil-wet rock.

2. Water saturation at which oil and water relative permeabilities are equal is generally greater than 50% for water-wet cores and less than 50% for oil-wet ones.

3. The relative permeability to water at floodout is generally less than 30% in water-wet rocks, but from 50 to 100% in oil-wet ones.

These relative permeabilities are based on the oil permeability at the connate water saturation. Examples of relative permeability curves in strongly water-wet and oil-wet cores taken from Craig⁷ are given in Fig. 6. Note that Raza *et al.*¹⁶ state that there are exceptions to the general rule that the connate water saturation is higher for a water-wet rock than for an oil-wet one.

Treiber *et al.*²⁷ proposed a second qualitative technique for strongly wetted rocks. The method compares the oil/water, gas/oil, and gas/water relative permeabilities and takes advantage of the fact that relative permeability of the strongly wetting phase is a function only of its own saturation.^{7,76,77} For example, if the sample is strongly water-wet, the relative permeability to oil (the preferential wetting phase with respect to the gas) in the gas/oil relative permeability test should be a continuation of the relative permeability to the water (the wetting phase) in the water/oil relative permeability test.⁷⁶ If significant differences are observed, the sample is not strongly water-wet.

An example of the comparison of the relative permeability curves in a strongly water-wet core taken from Owens and Archer⁷⁶ is shown in Fig. 7. The gas/oil drainage relative permeability, where the oil is the strongly wetting fluid, is shown as the dotted lines. The water/oil relative permeability, where the water is the strongly wetting fluid, is shown as the solid lines. Note that the water relative permeability, where the wetting fluid saturation is increasing, is a continuation of the oil relative permea-

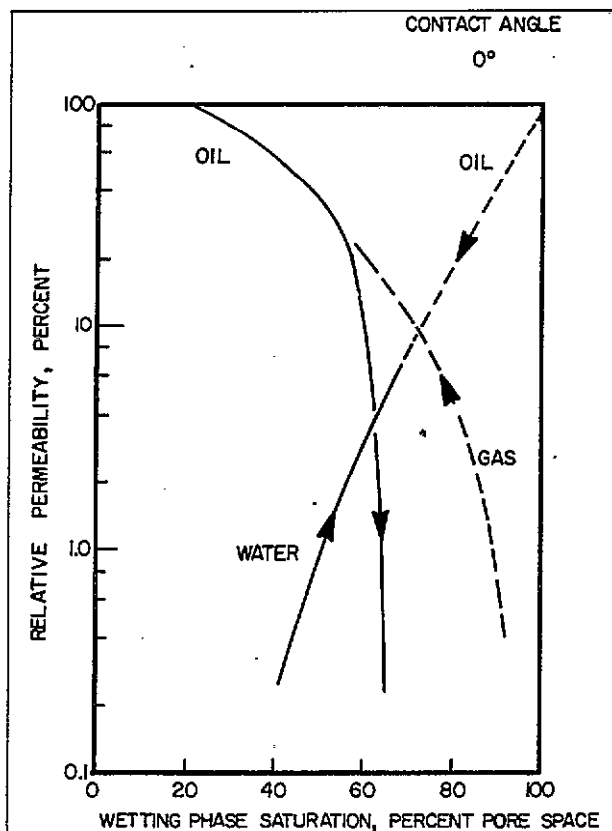


Fig. 7—Comparison of gas/oil drainage and water/oil imbibition relative permeability relationships. Torpedo sandstone.⁷⁶

bility, where the wetting fluid saturation is decreasing. This demonstrates that the core is water-wet.

Batycky *et al.*⁷⁸ developed a third wettability measurement technique that is based on unsteady-state relative permeability. Their method uses the capillary end effect that occurs when a core initially at IWS is waterflooded at a constant, slow injection rate. The end effect is the accumulation of wetting phase near the outlet end of the core caused by the discontinuity between the porous medium and the outlet pipe.⁷⁹ An increased pressure drop can occur because of this wetting fluid accumulation. Batycky *et al.*'s relative-permeability/wettability tests are run at very slow flow rates, so end effects are very important in determination of the pressure drop across the core. In contrast, standard unsteady-state relative permeability measurements use high flow rates to minimize the end effect.

Batycky *et al.* determined the wettability by waterflooding the core at very low rates until the ROS was reached. The flow was stopped to allow the fluid to redistribute, then restarted in the reverse direction. The core is water-wet if there is no change in the pressure drop after the flow reversal and oil-wet if the pressure drop is reduced immediately after the reversal. In a water-wet core at ROS, the wetting fluid saturation will be high throughout the core, with no additional water accumulation at the outlet end.^{78,80} There will be no redistribution of fluids when the flow is stopped; consequently, the pressure drop will not change. On the other hand, if the core is oil-wet, capillary forces will cause oil (the wetting phase) to accumulate near the outlet. The pressure drop caused by

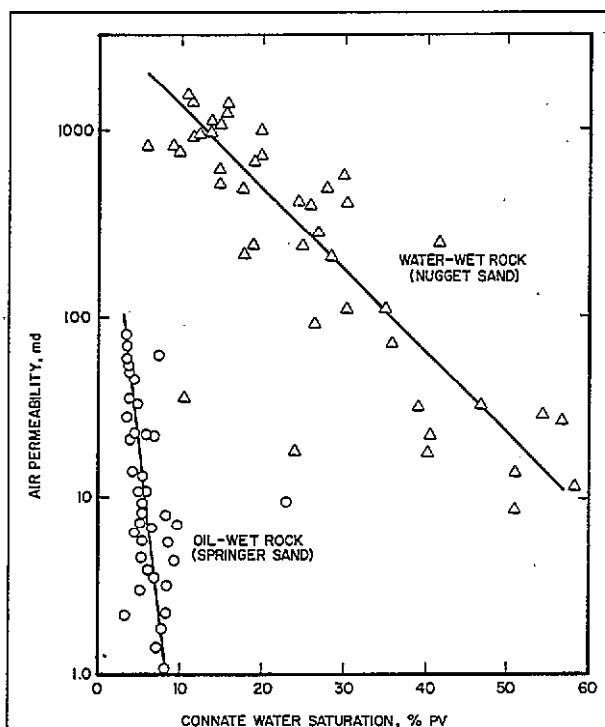


Fig. 8—Relationship between connate water saturation and air permeability.¹⁶

this oil accumulation is detected by stopping the flow, thereby allowing capillary forces to redistribute the oil evenly throughout the core. When flow is started in the reverse direction, the pressure drop will initially be lower, gradually rising to its original value as the end effect is re-established on the opposite end of the core.

Permeability/Saturation Relationships. Two qualitative methods based on air permeability and fluid saturations have been proposed. Both methods are statistical, require a relatively large number of samples, and give only a very rough idea of the wettability. The advantage of the methods is that only routine core analysis measurements are required. However, the reliability of these methods is unknown. The methods are also limited to core samples without significant fractures or vugs, in which the pore structure determines the air permeability.

Raza *et al.*¹⁶ proposed an empirical method to determine reservoir wettability based on connate water saturation and air permeability. To obtain the connate water saturation, core is obtained with an oil-based drilling fluid, then the freshly cut cores are analyzed for their water content. The cores are extracted and dried, and the air permeability is measured. A qualitative measure of the wettability is obtained by plotting the connate water saturation vs. the air permeability. Fig. 8 shows examples of the plot for strongly oil-wet and strongly water-wet conditions.¹⁶ For the oil-wet case, the average connate water saturation is generally relatively low. The curve is nearly vertical and extends over only a small saturation interval. Conversely, for the water-wet reservoir, the curve

has a gentle slope and extends over a large saturation interval.

Frehse⁸¹ proposed a second statistical method based on the assumption that low-permeability core samples will have a higher wetting-phase saturation than the high-permeability ones. For a uniformly wetted rock, the small pores are filled with the wetting fluid, while the large pores contain both the wetting and nonwetting fluids. In comparison to higher-permeability samples, a low-permeability sample will generally have a pore structure containing a larger number of small pores that are filled with the wetting fluid. To determine the wettability, Frehse classifies the routine core analysis samples into different permeability ranges. The saturation distributions for the highest and lowest permeability ranges are then compared. For example, consider a core taken with a water-based mud, where the residual oil saturations are known. The reservoir is assumed to be oil-wet if the low-permeability samples have a higher average ROS and water-wet if the high-permeability samples have a higher oil saturation. Currently, this method appears to be theoretical only. We are not aware of any tests comparing the results of this method with more standard wettability measurements, such as the Amott or USBM indices.

We feel that wettability evaluations based on air permeability and fluid saturations should not be used at present. Raza *et al.*'s method is empirical, and it is not known whether it is generally valid. Frehse's method has not been tested. Until these methods are evaluated by comparison with standard wettability measurements, they should be considered unreliable.

Grigor'ev⁸² proposed a theoretical method for determining an apparent contact angle based on the IWS and ROS. The method is probably not generally valid. It is based on a large number of unproven assumptions about the behavior of the water/oil/rock system. In addition, there do not appear to be any tests comparing this method with other wettability measurements.

Capillary Pressure Curves. As far back as 1951, Calhoun⁸³ suggested that the entire capillary pressure curve should be used to measure the wettability of the core. Gatenby and Marsden⁸⁴ were the first to examine the use of the areas under the capillary pressure curves for this purpose. The capillary pressure curves used were the complete drainage and imbibition curves for both positive and negative capillary pressures measured by the porous plate method. The two areas that they examined were the total area surrounded by the drainage and imbibition capillary pressure curves and the area under the oil-drive curve. They found that neither of these areas correlated well with the wettability of the core. However, Donaldson *et al.*⁹ later showed that the areas that should be measured were the areas under both the oil-drive and brine-drive curves. This is the basis of the quantitative USBM method discussed earlier.

Capillarimetric Method. Johansen and Dunning⁸⁵⁻⁸⁷ developed a qualitative wettability measurement that measured the adhesion tension, $\sigma \cos \theta$, in a glass capillary tube. In this capillarimetric method, the top of the tube is connected to a column filled with oil, while the bottom is connected to a column filled with water (see Fig. 9). The top of the water column can be raised or lowered rela-

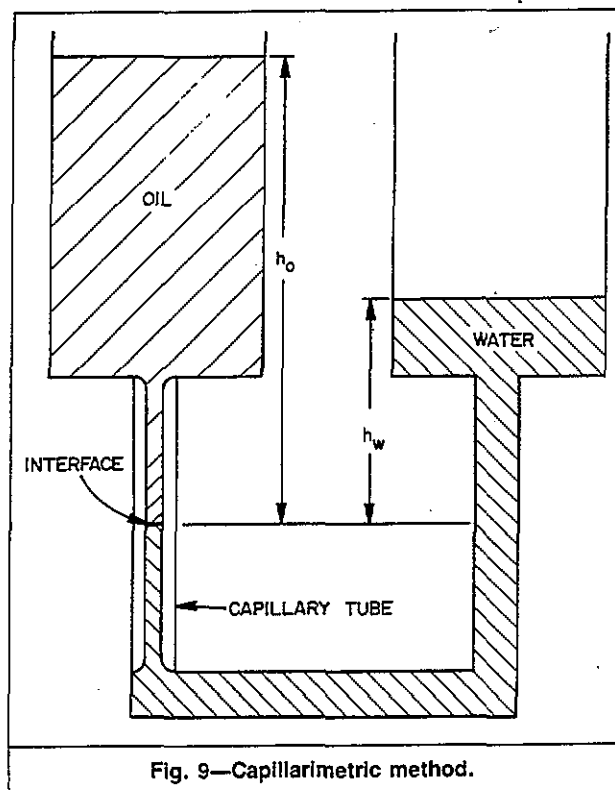


Fig. 9—Capillarimetric method.

tive to the oil column, changing the hydrostatic head. As the hydrostatic head is changed, the oil/water interfaces will rise or fall in the tube until the capillary forces balance the gravitational forces:

$$P_c = \frac{2\sigma \cos \theta}{r} = g(\rho_o h_o - \rho_w h_w), \quad \dots \dots \dots (7)$$

where

- r = radius of the capillary tube,
- ρ_o = oil density,
- ρ_w = water density,
- h_o = height of the oil column above the oil/water interface, and
- h_w = height of the water column above the oil/water interface.

Eq. 7 can be rearranged to calculate the product of σ and $\cos \theta$, which Johansen and Dunning called the displacement energy (adhesion tension):

$$E_D = \sigma \cos \theta = \frac{rg}{2}(\rho_o h_o - \rho_w h_w). \quad \dots \dots \dots (8)$$

The displacement energy is positive if water wets the glass and negative if oil wets it. If one of the liquids completely wets the glass, then the contact angle is zero, $\cos \theta$ is unity, and the displacement energy is equal to the IFT. Johansen and Dunning usually changed the height of the water column so that the interface moved over an area previously covered by oil; hence the contact angle in Eq. 8 is water advancing. The capillarimetric method assumes that glass is representative of the reservoir rock and there-

fore is generally only qualitative. Because this method measures the product $\sigma \cos \theta$, the problems discussed in the section on contact angles also hinder this method.

Displacement Capillary Pressure. One of the earliest wettability measurements was the displacement capillary pressure method, which uses the threshold capillary pressure to calculate an apparent contact angle.⁸⁸⁻⁹⁴ This method is now used infrequently, however, because pore geometry effects can cause the calculated contact angle to differ greatly from the contact angle measured on a flat plate.³ The displacement (or threshold) capillary pressure is the capillary pressure at which nonwetting fluid will first enter a core initially 100% saturated with the preferentially wetting fluid. An apparent contact angle is calculated from the threshold capillary pressure by modeling the rock as a straight, cylindrical capillary tube^{4,10}:

$$P_T = \frac{2\sigma \cos \theta_a}{r_{\max}}, \dots\dots\dots (9)$$

where P_T is the displacement capillary pressure, σ is the IFT, θ_a is the apparent contact angle, and r_{\max} is the radius of the pore through which the nonwetting fluid begins to enter the core. Because the capillary pressure needed to inject nonwetting fluid is reduced as the pore radius is increased, r_{\max} is an average of the radii of the largest pores in the core. Note that one limitation of this method is that it examines the wettability of only the largest pores. Because Eq. 9 has two unknowns, θ_a and r_{\max} , the only way to solve for the apparent contact angle is to make additional assumptions. It is usually assumed that some fluid exists that will completely wet the core, so $\cos \theta = 1$, and r_{\max} can be calculated. This allows the contact angle to be computed for other fluid pairs.

Slobod and Blum⁹³ proposed two semiquantitative wettability measurements based on the displacement capillary pressure, the wettability number, and the apparent contact angle. The wettability number is calculated by carrying out two displacement experiments—first, water by oil, and second, oil by air. Eq. 9 for the oil/water/rock system becomes

$$P_{(o-w)T} = \frac{2\sigma_{o-w} \cos \theta_{o-w}}{r_{\max}} \dots\dots\dots (10a)$$

and for the air/oil/rock system,

$$P_{(a-o)T} = \frac{2\sigma_{a-o} \cos \theta_{a-o}}{r_{\max}} \dots\dots\dots (10b)$$

In both equations, the radius of the pore is assumed to be the same. The wettability number, N , is determined by solving Eq. 10 for the ratio of the $\cos \theta$ terms:

$$N = \frac{\cos \theta_{o-w}}{\cos \theta_{a-o}} = \frac{\sigma_{a-o} P_{(o-w)T}}{\sigma_{o-w} P_{(a-o)T}} \dots\dots\dots (11)$$

Slobod and Blum stated that if it were assumed that the oil is completely wetting in the oil/air/rock system, then $\cos \theta_{a-o}$ is unity. An apparent contact angle for the oil/water system can then be computed from Eq. 11:

$$\cos(\theta_{o-w})_a = \frac{\sigma_{a-o} P_{(o-w)T}}{\sigma_{o-w} P_{(a-o)T}} \dots\dots\dots (12)$$

Slobod and Blum realized that their assumptions were only approximately true and that the contact angle that could be calculated from the displacement pressure was, at best, only semiquantitative. In general, the apparent contact angle measured from the displacement pressure is not equal to the contact angle measured on a smooth surface because of pore geometry effects. Morrow and his coworkers⁴³⁻⁴⁵ compared apparent contact angles computed in sintered teflon cores using pure fluid with the true contact angles measured on a smooth teflon plate. There was no change in the apparent contact angle when the true contact angle was varied from 0 to 22° [0 to 0.4 rad]. In addition, when θ was greater than 22° [0.4 rad], the apparent contact angle was always less than the true contact angle. Finally, in some cases, the apparent contact angle calculated from the displacement pressure can show the wrong fluid to be the wetting phase. Positive displacement pressures for both fluids, particularly when the core is initially 100% saturated with the other fluid, have been frequently reported in the literature.^{41,45,83,90,92,95-97} When a positive displacement pressure is required for both fluids, the fluid with the lower displacement pressure is the preferentially wetting fluid because less energy is required to force it into the core.^{83,98} Anderson³ provides further discussion.

Reservoir Logs. Graham⁹⁹ proposed a method to measure the wettability of in-situ reservoir rock with logs that was based on the fact that the electrical resistivity of an oil-wet rock is higher than that of a water-wet rock at the same saturation.² In Graham's method, the formation is injected with brine, and resistivity logs are run. The formation is then injected with the same brine containing a reverse wetting agent, which will change a water-wet formation to an oil-wet one; if the formation is already oil-wet, the reverse wetting agent will not alter the wettability. After logs are rerun, the wettability of the formation can be determined by comparing the two resistivity measurements. If the formation was originally water-wet, the change to oil-wet will increase the resistivity. If the formation was oil-wet, no change in resistivity will be observed.

Holmes and Tippie¹⁰⁰ proposed a second method that compares logs with core data. The saturation in a formation is first measured with logs and the data converted into a capillary pressure curve. Next, the capillary pressure is measured in a clean water-wet core where it is assumed that the contact angle is zero, and the two capillary pressure curves are compared. If they agree, the reservoir is strongly water-wet. If they do not agree, Holmes and Tippie model the porous medium as a series of straight cylindrical capillaries and determine the apparent contact angle with equations similar to those discussed in the previous section on displacement capillary pressure. Because of the number of approximations, this

apparent contact angle will provide only a rough estimate of the actual reservoir wettability.

Measurement of Fractional and Mixed Wettability

In fractional wetted cores, a portion of the rock is strongly water-wet, while the rest is strongly oil-wet. The term "mixed wettability" was introduced by Salathiel¹⁰¹ to refer to a special type of fractional wettability in which the oil-wet surfaces form continuous paths through the larger pores. Additional information can be found in Ref. 1.

Nuclear Magnetic Relaxation. Brown and Fatt¹⁰² and others^{103,104} proposed a nuclear magnetic resonance (NMR) method for determining the fraction of the core that is oil-wet vs. water-wet in a core with fractional wettability. The method uses the nuclear magnetic thermal relaxation time for water protons (hydrogen) in porous media. To measure the relaxation time, the sample is first exposed to a strong magnetic field, which makes the nuclei of the hydrogen atoms line up with the field. The core is then exposed to a much weaker field. The nuclear magnetic relaxation time, which is the time it takes for the hydrogen nuclei to adjust (relax) to the new field, is measured. There are two relaxation times: relaxation of the component parallel to the field is called "thermal relaxation," and relaxation of the component perpendicular to the field is called "transverse relaxation."¹⁰⁵ The thermal relaxation time is the time used to measure fractional wettability.

For thermal relaxation to occur after the magnetic field is changed, the protons must dissipate some of their energy to random thermal motion of the molecules. The protons are only loosely coupled to their environment, so they require a time on the order of seconds to adjust to the new magnetic field, which is a very long time for atomic processes.

The use of nuclear magnetic relaxation times to measure wettability is based on the observation that the surfaces of the porous media can significantly reduce the measured relaxation time.^{102,105} When a proton is near a surface, it can become temporarily bound to the surface, relaxing much faster than in the bulk fluid. The wettability of the surface can influence the relaxation time.¹⁰²⁻¹⁰⁵ Oil-wet surfaces cause a smaller reduction in relaxation time than water-wet surfaces.

Brown and Fatt¹⁰² examined 100% water-saturated sand packs in which a fraction of the sand grains were water-wet and the remainder had been treated with an organochlorosilane to render them oil-wet. They found a linear relation between the relaxation rate and the fraction of oil-wet surface area. (The relaxation rate is the inverse of the relaxation time.) The greater the fraction of oil-wet grains, the longer the relaxation time, and the slower the relaxation rate. Kumar *et al.*¹⁰⁴ measured relaxation times with 100% water-saturated bead packs composed of water-wet glass beads and non-water-wet polymethylmethacrylate beads. The relaxation time increased linearly as the fraction of non-water-wet beads increased.

Brown and Fatt¹⁰² and Kumar *et al.*¹⁰⁴ applied their method only to sandpacks and beadpacks. Devereaux¹⁰³

found that asphaltene adsorption in sandstone cores could also increase the relaxation time. In one set of experiments, clean sandstone plugs were saturated with crude oil, then aged for several days. The bulk of the oil was removed by flushing with cyclohexane, leaving behind a film of asphaltenes on the rock surfaces. The plugs were saturated with water, and the relaxation time measured. The adsorbed film increased the relaxation time when compared with the time for clean plugs. In another experiment, a plug was saturated with water and crude, aged, flushed with cyclohexane, then saturated with water. The nuclear magnetic relaxation curve for this sample had three components: (1) a fast component for water in the small pores, (2) an intermediate component for water in the large pores, and (3) a slow component for water in the large pores that had been filled with oil and coated with asphaltenes. However, Devereaux did not suggest any way to use this to measure the wettability.

Brown and Fatt¹⁰² also proposed a nuclear magnetic relaxation method to measure the wettability of reservoir core, which apparently has not actually been used. The method compares the nuclear magnetic thermal relaxation rate of the untreated core with reference measurements on the same core in both strongly water-wet and strongly oil-wet states. The core is first flushed with toluene or hexane to displace all of the brine and oil. After vacuum drying, the core is saturated with distilled water, and the thermal relaxation rate is measured. It is assumed that the preparation procedure above has not altered the wettability of the core. Next, the core is made strongly water-wet by flushing with methanol and chloroform or by firing at 950°F [510°C] to remove all of the adsorbed surface material. The nuclear magnetic thermal relaxation rate of the core in this water-wet reference state is measured. Finally, the core is treated with an organochlorosilane, which renders it strongly oil-wet, and the thermal relaxation rate is measured. The reference relaxation rates for the core when it is strongly water-wet and oil-wet are plotted vs. the percent of oil-wet surface, and a straight line is drawn between them. Assuming a linear relationship between fractional wettability and relaxation rate, the fractional wettability of the native-state untreated core is then found by plotting its relaxation rate on this straight line.

Unfortunately, this proposed procedure suffers from several problems. First, the functional relationship between relaxation rate and fractional wettability is not clear. Brown and Fatt found a linear relationship between fractional wettability and reaction rate, while Kumar *et al.* found a linear relationship using reaction time (the inverse of reaction rate). Second, as discussed in Anderson,¹ the methods that Brown and Fatt suggest to prepare the original core will generally alter the native-state wettability. Finally, it is not possible to tell whether the cleaning method has rendered the core totally water-wet or the organochlorosilane treatment has rendered the core totally oil-wet. In some cases, core treated with an organochlorosilane is only neutrally wet.¹

Dye Adsorption. Holbrook and Bernard¹⁰⁶ used the adsorption of methylene blue from an aqueous solution injected into a core to measure fractional wettability. This method successfully measured the wettability of fraction-

ally wetted sandpacks containing mixtures of oil-wet and water-wet sands. However, the method will probably not work for reservoir cores containing large amounts of clay.

In this method, water-covered rock surfaces are assumed to be water-wet, while the oil-covered ones are assumed to be oil-wet. The technique is based on the observation that a rock surface covered with water will adsorb a large amount of methylene blue, whereas one covered with oil will not. The dye adsorption of the test core is measured at ROS, where essentially all of the wetting phase is continuous.¹⁰⁷⁻¹¹⁰ This enables the dye to adsorb on essentially all of the water-covered, water-wet surfaces. A reference dye adsorption measurement is made on an adjacent core plug that is cleaned to render it totally water-wet. The cleaned reference plug is saturated with brine, so the entire rock surface is water-covered. The fractional wettability is then established by dividing the dye adsorption of the test core by that of the 100% water-wet reference core. When this method was tested on fractionally wetted sandpacks containing mixtures of oil-wet and water-wet sands, a linear relationship between the fractional wettability and the dye adsorption was found.

The dye adsorption test actually measures the fraction of the total surface area of the core that is contacted by the injected water. Because of this, both oil and water must be present in the core when the dye adsorption is measured. The dye adsorption method makes two additional assumptions: the water phase is continuous at ROS, so the dye contacts all of the water-covered surfaces; and the thin films of oil and water coating the rock surfaces are not affected by large changes in saturation. Tracer experiments have shown that essentially all of the water is continuous at ROS for both water-wet and oil-wet cores.¹¹⁰ The assumption that the thin films of oil and water are not affected by large changes in saturation seems reasonable because the amount of liquid in the thin films is very small in comparison with the bulk fluids. Shankar and Dullien¹¹¹ examined how dye adsorption varied with water saturation in Berea sandstone cores. They injected oil and brine at constant rates and allowed the saturations in the core to reach equilibrium. The injection was then switched from brine to dyed brine, and the dye adsorption was measured. They found that the dye adsorption was almost constant when the water saturation was greater than 40% PV. The dye adsorption decreased at lower saturations, where the water started to lose continuity. These measurements show that the wettability of a core measured by dye adsorption is not dependent on the saturation, except possibly at water saturations near IWS.

Although the fractionally wetted sandpacks that were used by Holbrook and Bernard did not contain clays, they realized that clays would strongly affect dye adsorption in reservoir cores. This occurs because the surface area and dye adsorption capacities of clays are much larger than those of sand grains.^{111,112} Holbrook and Bernard stated that their test would measure the fraction of the clay surface that was water-wet in a reservoir core. However, they had problems when measuring the dye adsorption and fractional wettability of cores containing a significant amount of montmorillonite. Irreversible changes in the clay structure of the water-wet reference core resulting from extraction and drying caused them to calculate relative water wettabilities that were greater than 100%. Note,

however, that it may be possible to use supercritical drying to avoid these problems.¹¹³

Mixed Wettability. At the current time, there is no single wettability test that will determine whether a core has Salathiel's¹⁰¹ mixed wettability. It appears possible, however, to make this determination by examining the results of (1) a glass slide wettability test, (2) a waterflood of the native-state core, and (3) several waterfloods of restored-state cores that were aged with different brine saturations. As discussed in the introductory paper,¹ in a mixed-wettability core, the oil-wet rock surfaces form continuous paths throughout the large pores, while the smaller pores remain water-wet. Mixed wettability can occur in a rock if the crude forms a thick oil-wet layer on the surface only in those places where it is in direct contact. This can be tested with the glass slide method, with half the slide in crude and the other half in brine. Quartz or calcite crystals could also be used to give a surface more representative of the reservoir. The core may have mixed wettability if the half of the slide aged in crude forms a thick, oil-wet layer, while the half aged in brine remains water-wet. If the entire slide remains water-wet or becomes oil-wet, the core will probably have a uniform wettability.

The second measurement to indicate mixed wettability is a waterflood of the native-state core. If the core has mixed wettability, oil will be produced down to a very low ROS as many PV's of water are injected. Uniform-wettability cores will generally have a shorter duration of production and/or a larger ROS.^{6,7,114,115} Finally, a series of waterfloods in restored-state cores can be used to confirm the mixed wettability of the core. A series of cores is cleaned, saturated in brine, oilflooded with crude to different brine saturations, then aged to restore its original wettability. Salathiel found that the recovery from his restored-state mixed-wettability cores had a maximum at a particular value of the brine saturation during aging. When the water saturation was lower than this value, some of the small pores became oil-wet, lowering recovery. Conversely, at larger water saturations, the oil pathways through the core became discontinuous.

Two other measurements that will sometimes help in determining whether a core has mixed wettability are imbibition measurements and capillary pressure behavior.³ Spontaneous (free) imbibition of both oil and water has been reported for some cores with fractional or mixed wettability.⁴⁹⁻⁵¹ These cores will have positive displacement-by-water and displacement-by-oil ratios. Another indicator of mixed wettability is a comparison of oil-displacing-brine capillary pressure measured on native-state plugs vs. measurements on the same plugs after they have been cleaned and rendered water-wet. In some mixed-wet plugs, the native-state capillary pressure curve will cross over the cleaned curve as the capillary pressure is increased.¹¹⁶⁻¹¹⁸ Further discussion can be found in Ref. 3.

In summary, if the oil forms thick, oil-wet films only on those portions of the glass slide with which it is in direct contact; if the core can be flooded down to very low oil saturation, yet still produce small amounts of oil; and if the oil recovery from a restored-state core has a maximum at a specific brine saturation during its aging period, then the core likely has mixed wettability. Imbibition

and capillary pressure measurements can also help determine whether a core has mixed wettability.

Conclusions

1. Three quantitative wettability measurements are in use today: contact angle, the Amott method, and the USBM method. The contact angle measures the wettability of crude and brine on a polished mineral surface. It is the best method to use when pure fluids and artificial cores are used. It is also used to examine the effects on wettability of experimental conditions, such as pressure, temperature, and brine chemistry. The USBM and Amott methods measure the average wettability of core. They are superior to the contact-angle method when the wettability of native- or restored-state core is measured. They also must be used to determine whether a core has been cleaned completely. The USBM method appears to be superior to the Amott method, which is insensitive near neutral wettability. A modification of the USBM method, developed by Sharma and Wunderlich,⁵⁷ allows the calculation of both the USBM and Amott wettability indices.

2. A large number of qualitative wettability measurement methods are available. The imbibition method is the most widely used because it is fast, does not require any complicated equipment, and gives an idea of the average wettability of the core. The microscope examination method is often used in flow visualization studies. Finally, wettability measurement methods based on relative permeability curves are often used when these data are available.

3. Two methods have been developed to measure the fractional wettability: the NMR method and the dye adsorption method. Neither method is widely used today.

4. There is no method to determine whether a core has mixed wettability. However, it appears that it may be possible to make such determination by examining the results of a glass slide wettability test, a waterflood of the native-state core with many PV's of water, several waterfloods of restored-state cores that were aged with different brine saturations, and imbibition and capillary pressure measurements.

Nomenclature

- A_1 = area under the oil-drive centrifugal capillary pressure curve, USBM method
- A_2 = area under the brine-drive centrifugal capillary pressure curve, USBM method
- E_D = displacement energy (adhesion tension)
- g = acceleration of gravity
- h_o = height of the oil column above the oil/water interface
- h_w = height of the water column above the oil/water interface
- I = Amott-Harvey relative displacement index
- \dot{m} = initial imbibition rate of a core just after it is submerged in a fluid
- \dot{m}_r = initial imbibition rate of a core after it is cleaned and rendered strongly water-wet
- N = wettability number, Eq. 11
- P_c = capillary pressure
- r = capillary tube radius

- r_{\max} = computed equivalent circular radius of the largest pores in a core, Eq. 9
- R = relative rate of imbibition, Eq. 6
- V_{osp} = volume of oil displaced by spontaneous imbibition of water, Amott method
- V_{ot} = total volume of oil displaced, Amott method
- V_{wsp} = volume of water displaced by spontaneous imbibition of oil, Amott method
- V_{wt} = total volume of water displaced, Amott method
- W = USBM wettability index
- δ_o = displacement-by-oil ratio, Amott method
- δ_w = displacement-by-water ratio, Amott method
- θ = contact angle
- ρ_o = oil density
- ρ_w = water density
- σ = IFT
- σ_A = adhesion tension
- σ_{os} = interfacial energy between the oil and solid
- σ_{ow} = interfacial energy between the oil and water
- σ_{ws} = interfacial energy between the water and solid

Subscripts

- a = apparent
- adv = advancing
- $a-o$ = air-oil
- $o-w$ = oil-water
- rec = receding
- T = threshold

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SI Metric Conversion Factors

degrees	× 1.745 329	E-02	= rad
°F	(°F-32)/1.8		= °C
psi	× 6.894 757	E+00	= kPa

JPT

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Wettability Literature Survey—Part 3: The Effects of Wettability on the Electrical Properties of Porous Media

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13934

Summary. This paper examines the effects of wettability on the Archie saturation exponent and the formation factor, which are determined experimentally in cores. These parameters are important in the investigation of the hydrocarbon saturation of a formation by use of resistivity data obtained from well logging. The Archie saturation exponent, n , typically has a value of about 2 in water-wet formations and cleaned cores, while in native-state, non-water-wet cores and formations it is generally larger than 2. In uniformly oil-wet cores with low brine saturations, n can reach values of 10 or more. The exponent is higher in oil-wet cores at low saturations because a portion of the brine is trapped or isolated in dendritic fingers where it is unable to contribute to electrical conductivity. If a cleaned water-wet core is used to measure n and the reservoir is actually oil-wet, interstitial water will be underestimated during logging. No definite conclusions can be drawn about the effects of wettability on the formation factor. However, the wettability of clays in a core is likely to affect this parameter.

Introduction

This paper is the third in a series on the effects of wettability on core analysis.¹⁻³ Changes in the wettability of the core have been shown to affect electrical properties, capillary pressure, waterflood behavior, relative permeability, dispersion, tertiary recovery, irreducible water saturation, and residual oil saturation. For core analysis to predict the behavior of a reservoir, the wettability of the core must be the same as the wettability of the undisturbed reservoir rock.

In the first report,¹ the various kinds of wettability, such as mixed wettability, were discussed. That paper also defined native-state, cleaned, and restored-state cores and gave the procedures necessary to obtain each type. Note that a restored-state core has been cleaned and then aged with native crude oil and brine at reservoir temperature until the native wettability is restored. This definition is used in the majority of the more recent literature. Be aware, however, that in some papers, particularly older ones, the term "restored state" is used for what are actually "cleaned" cores (e.g., see Craig⁴).

Wettability and saturation history are important factors in the determination of the electrical resistivity of a porous medium because they control the location and distribution of fluids. The electrical resistivity of a core is determined by the lengths and cross-sectional areas of the conducting paths through the brine. Large resistivity is caused by small cross-sectional areas and long conduction paths. First, consider a 100% brine-saturated core. The resistivity of the core is much higher than the resistivity of an equivalent volume of brine because the nonconductive rock reduces the cross-sectional area through which the current can flow. At the same time, the rock increases the length of the conducting paths.

The resistivity of the core is increased further by any hydrocarbon saturation in the core because hydrocarbons are also nonconductive. The increase will depend on the saturation, wettability, and saturation history, the factors that control the location and distribution of the oil and water in the rock. In a water-wet rock, the brine occupies the small pores and forms a continuous film on the rock surfaces. In an oil-wet rock, the brine is located in the centers of the larger pores. This difference in brine distribution caused by the wettability becomes very important as the brine saturation is lowered. Generally, almost all of the brine in the water-wet rock remains continuous, so the resistivity increases because of the decrease in the cross-sectional area that can conduct flow. In an oil-wet rock, a portion of the brine will lose electrical continuity as the saturation is lowered, so the electrical resistivity will increase at a faster rate.

Effects of Wettability on Resistivity and the Archie Saturation Exponent

The hydrocarbon saturation of a formation is often estimated from resistivity data obtained by well logging. The empirically determined Archie⁵ saturation equation is often used:

$$S_w^{-n} = \frac{R_t}{R_o} = I_R, \dots \dots \dots (1)$$

where

S_w = brine saturation in the porous medium,

R_t = resistivity of the porous medium at saturation S_w , and

R_o = resistivity of the 100% brine-saturated formation.

The ratio of the two resistivities is called I_R , the resistivity index. The Archie saturation exponent, n , is a dimensionless empirical parameter that is determined experimentally from core plugs. The value of n depends on the formation but usually has a value of about 2 for water-wet formations and cleaned water-wet cores.

Oil-Wet vs. Water-Wet Cores. Mungan and Moore⁶ have pointed out that the Archie saturation equation makes three implicit assumptions: (1) the saturation/resistivity relation is unique, so only one resistivity will ever be measured at a given saturation; (2) n is constant for a given porous medium; and (3) all the brine contributes to the flow of electric current. It has been shown that these assumptions are valid only when both the reservoir and core are strongly water-wet because n depends on the distribution of the conducting phase in the porous medium and therefore depends on the wettability. If the wettability is altered, the change in the spatial distribution of the fluids alters the lengths and cross-sectional areas of the conductive paths, which in turn changes the resistivity. Hence the Archie equation is nonunique when the wettability is altered because different resistivities can be measured at the same saturation.

The experiments discussed below show that n can be a great deal higher in oil-wet than in water-wet rocks. Morrow⁷ provides additional discussion. Because the saturation exponent depends on the wettability, n must be measured at reservoir wetting conditions, or invalid saturations will be obtained from logs. For example, if n is measured in a cleaned water-wet core and the reservoir is actually oil-wet, the water saturation in the reservoir would be underestimated. Pirson and Fraser⁸ cite an example of a well in an oil-wet reservoir that produced only water. Assuming a water-wet reservoir, logs in this same well indicated an interstitial water saturation of only 25%.

The effects of wettability on the Archie saturation exponent become more important as the brine saturation decreases because, in an oil-wet system, there is more disconnection and isolation of globules of brine. The isolated brine is surrounded by oil, which acts as an insulator and causes this brine to be unable to conduct a current flow. First, consider a water-wet system initially at a high brine saturation. The brine is located in the small pores and as a thin layer on the rock surfaces, while the oil is located in the center of the larger pores. All the brine is continuous and can conduct current. As the water saturation is lowered to the irreducible water saturation (IWS), essentially all of the brine in a water-wet system remains continuous and conductive, allowing the saturation exponent to remain about 2. This continuity at all saturations above IWS has been demonstrated experimentally by steady-state miscible floods. These floods show that generally, there is little or no trapping or isolation of any of the brine by oil.⁹⁻¹² This implies that most of the increase in the resistivity is caused by the decrease in the cross-sectional area available for conduction, not by increases in the path length or brine trapping.

In a uniformly oil-wet system, the oil is located in the small pores and on the rock surfaces, while the brine is located in the center of the larger pores. At high brine saturations, the brine is continuous, just as it is in a water-wet system, even though its location is different. For this

situation, the Archie resistivity/saturation relation behaves as it does in the water-wet case, with n around 2. In contrast to the water-wet case, however, as the brine saturation decreases, a portion of the brine no longer contributes to the current flow. In some experiments, the saturation exponent increases as soon as the brine saturation is decreased, while in others the brine saturation must be reduced to about 35% before n increases. At very low water saturations (<35%), large values of the saturation exponent, $n \geq 10$ can occur.

Two factors can cause the resistivity, and hence n , to rise more rapidly compared with the water-wet case: the trapping of a portion of the brine by oil, and the formation of dendrites or fingers of brine.¹³ As stated previously, these factors decrease the cross-sectional area and increase the length of the conducting paths, thereby increasing electrical resistivity. Flow visualization and steady-state miscible experiments demonstrate that a significant fraction of the nonwetting phase becomes disconnected as the nonwetting phase saturation decreases.^{4,12,14-17} This isolated brine is surrounded by nonconducting oil and cannot contribute to the current flow. As the brine saturation is reduced, the electrical resistivity will also be increased because some of the brine will be located in pseudo-dead-end pores,^{17,18} also known as fingers or dendritic structures. These fingers consist of brine that is connected to the continuous brine in only one location. The brine cannot conduct electricity because of the oil/water interfaces in the remainder of the pore throats, so the length of the conducting paths is increased.

Note that the volume of nonconducting dendrites is not the same as the dendritic fraction measured in steady-state miscible flooding experiments. The dendritic fraction in a miscible experiment is a measurement of the brine that is continuous but does not flow. In a water-wet system, this includes the nonflowing brine located in the small pores, as well as the brine in the fingers. On the other hand, the volume of nonconducting dendrites is a measurement of the brine that is continuous but nonconducting. These two volumes are different because the continuous brine in the small pores conducts electricity, while the brine in the fingers does not.

Experimental Measurements

The experimental systems used to study the effects of wettability on the saturation exponent can be divided into three types: (1) uniformly wetted systems; (2) reservoir cores, which may or may not have uniform wettability; and (3) fractional and mixed-wettability systems. In the first set of experiments with uniform wettability, the wettability of the entire core is varied from water-wet to oil-wet. At any given wettability, the wettability of the entire surface is kept as uniform as possible.

In many cases, reservoir core will not have uniform wettability. For example, the different minerals on the rock surface can have different surface chemistry and adsorption properties, possibly causing variations in wettability. The second set of experiments discussed is for reservoir cores. Several of these cores are native-state, where alterations to the reservoir wettability are minimized. Finally, the third set of experiments examines the wettability effects that occur when a core has fractional or mixed wettability, where some of the rock surfaces are

TABLE 1—ARCHIE SATURATION EXPONENTS AS A FUNCTION OF SATURATION FOR A CONDUCTING NONWETTING PHASE⁶

Air/NaCl Solution		Oil/NaCl Solution	
Brine Saturation (% PV)	<i>n</i>	Brine Saturation (% PV)	<i>n</i>
66.2	1.97	64.1	2.35
65.1	1.98	63.1	2.31
63.2	1.92	60.2	2.46
59.3	2.01	55.3	2.37
51.4	1.93	50.7	2.51
43.6	1.99	44.2	2.46
39.5	2.11	40.5	2.61
33.9	4.06	36.8	2.81
30.1	7.50	34.3	4.00
28.4	8.90	33.9	7.15
		31.0	9

strongly water-wet but the remainder are oil-wet. In these experiments, the effects of wettability are studied by variation of the location and the proportion of the surfaces that are water-wet vs. oil-wet.

Uniformly Wetted Systems. Mungan and Moore⁶ studied the effects of wettability on resistivity using both synthetic polytetrafluoroethylene (teflon) and natural cores. They found that *n* could be as high as 9 when the conductive liquid was the nonwetting phase. When it was the wetting phase, *n* was around 2 in the same core. The fluid pairs used in the teflon core were methanol/air, air/brine, and oil/brine. For the methanol/air case, methanol is both the wetting and conducting phase and is analogous to the brine in a water-wet rock. The saturation exponent was about 1.9, approximately what would be measured in a water-wet reservoir core with oil and brine. This demonstrates that the location and resistivity index of the fluids are similar in the two systems, oil/brine/reservoir rock and air/methanol/teflon, when the wetting liquid is also the conducting phase.

Next, Mungan and Moore used air/brine or oil/brine as the two fluids in the teflon core. The brine is then the conducting, nonwetting phase, behaving in a fashion similar to brine in an oil-wet core. The saturation exponents are shown in Table 1. An examination of Mungan and Moore's data shows what typically happens in an oil-wet system as the brine saturation is decreased. Above a certain conducting phase saturation, the exponent *n* is constant and near 2. Below this saturation, however, the exponent begins to increase rapidly.

By microvisual examination, Mungan and Moore found that portions of the brine in the teflon cores started to become disconnected when the brine saturation was lowered to about 35%. This disconnected brine did not conduct electrical current because it was completely surrounded by the insulating wetting phase (air or oil). Resistivity increased more rapidly as the brine saturation was lowered below 35%. Table 1 shows that the exponent begins to rise as the brine saturation drops below 40%, eventually increasing to about 9. Mungan and Moore concluded that the Archie saturation equation was not valid at low water saturations in an oil-wet rock. They pointed out, however, that a valid saturation-resistivity relationship could be empirically determined if the reservoir wettability were pre-

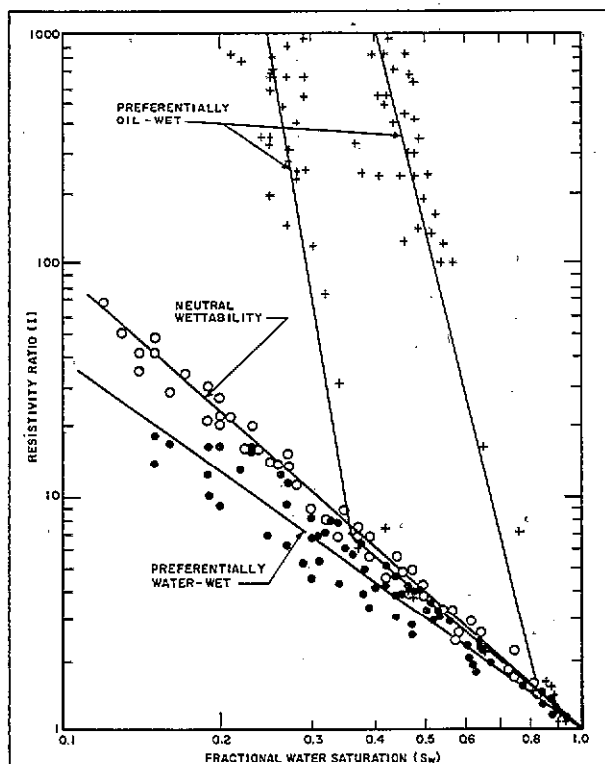


Fig. 1—Resistivity ratio vs. water saturation in carbonate cores.²⁰

served with a native-state core and reservoir fluids were used for the measurements.

Sweeney and Jennings^{19,20} measured the effects of wettability on carbonate cores. The cores were first extracted with toluene, which left them in a neutral-wettability state, as determined by the imbibition method.¹ This method is only qualitative, so the actual wettability of the core was somewhere between mildly water-wet and mildly oil-wet.

The electrical resistivity of the neutrally wet core was measured as a function of water saturation. The cores were then fired at 840°F [450°C] to remove all of the organic material present, rendering the core strongly water-wet. Note that this caused a slight increase in the porosity because of dissociation of a portion of the calcium carbonate into calcium oxide and carbon dioxide. After the new resistivity behavior was measured, the cores were treated with naphthenic acids to make them oil-wet. The resistivity behavior was measured again, and the results are shown in Fig. 1. The Archie saturation exponent, *n*, is the slope of each line. The saturation exponent of the water-wet cores was about 1.6, and for the neutrally wet cores about 1.9.

There were two different types of behavior for the cores once they had been rendered oil-wet. In some cores, the saturation exponent was high (about 8) even when the brine saturation was very high. The behavior of the remainder of the cores was similar to the water-wet and neutrally wet cores until a brine saturation of about 35% was reached. At this point, *n* increased rapidly to a value of about 12. This is similar to Mungan and Moore's⁶ findings. Sweeney and Jennings^{19,20} stated that the oil-wet carbonate cores could also be separated into the same two

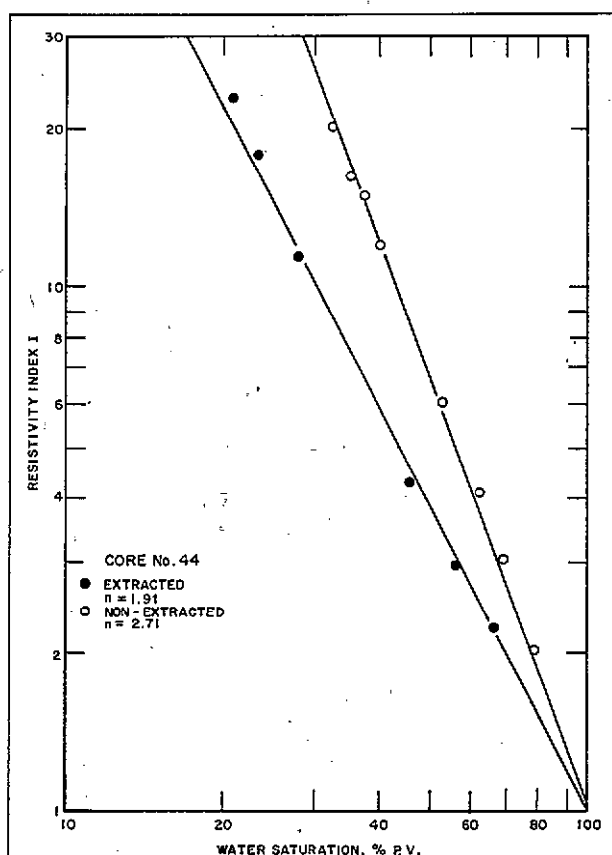


Fig. 2—Effect of cleaning on the Archie saturation exponent.²⁷

groups on the basis of pore-size distribution and petrographic analysis. Unfortunately, they give no details.

Rust²¹ compared the saturation exponent for oil and water in a cleaned sandstone before and after it had been treated with an organochlorosilane solution to render it mildly oil-wet. He found that the saturation exponent for the clean water-wet sandstone was about 1.7, while for the oil-wet sandstone it was about 13.5 even at high brine saturations. Unfortunately, Rust may have had problems with his experimental apparatus, indicated by saturation exponent values in the oil-wet sandstone of only 3.5 when air and water were used.

Keller,²² Licastro and Keller,²³ and Holmes²⁴ measured the resistivity of oil-wet and water-wet reservoir cores using air and brine. The results are very similar to the experiments described previously, even though core saturations were changed by evaporation, which possibly caused salinity variations. In addition, the fluid distribution may have differed from the distribution existing when oil and brine were used.

Goddard *et al.*¹³ measured the electrical resistivity of mercury, a nonwetting fluid, as a function of saturation in several sandstone plugs. Mercury was injected into the dry core and then withdrawn while the resistivity was measured. When the mercury was withdrawn from the sample, the resistivity was at first slightly less than the injection resistivity at the same saturation. It quickly became much higher than the injection resistivity as the mercury saturation was reduced, however, and was essentially infinite at a residual mercury saturation. Goddard *et al.*

TABLE 2—EFFECT OF CLEANING ON THE ARCHIE SATURATION EXPONENT²⁷

Core Number	Unextracted	Extracted
1	2.37	2.03
2	2.68	2.29
3	2.48	2.07
4	2.71	1.91
5	2.82	2.44
6	2.21	1.91
Average	2.55	2.11

state that these high values occur because a significant part of the nonwetting mercury was either trapped or located in dendrites where it could not contribute to the conductivity.

Zierfuss and Maltha²⁵ measured electrical resistivity during waterfloods of sandstone and limestone cores and artificial packs. Each porous medium was saturated with an aqueous ammonium thiocyanate solution ("water"), oilflooded, and then waterflooded. The wettability was controlled by treating the porous medium with different concentrations of naphthenic acids. As the system became more oil-wet, the waterflooding behavior was altered. At the same time, the resistivity at IWS was increased.

Reservoir Core. The experiments discussed previously showed the effects of wettability on the saturation exponent in uniformly wetted cores. Generally, either a teflon core was used or the entire core was treated with a chemical to make it oil-wet. The experiments in this section demonstrate that wettability is also a major control parameter in the determination of n in reservoir core. While the Archie saturation exponent will be higher than 2 in native-state oil-wet cores, it will generally not reach the very high values for uniformly wetted systems. Because of variations in mineral composition, many reservoir cores will probably have fractional (heterogeneous) wettability, making a portion of their surface water-wet. This will decrease the rate at which the water becomes disconnected at low water saturations and lower the saturation exponent.

In addition to measurements in uniformly wetted teflon cores, Mungan and Moore⁶ measured the resistivity of native-state reservoir cores that were known to be oil-wet and had an interstitial water saturation of 10%. The resistivity was too high to be measured, implying that most of the brine was disconnected. The cores were waterflooded and then oilflooded to 30% brine saturation, and values of n were measured. They varied from 2 to 3.5. Of course, at this higher brine saturation, the wettability effects were reduced.

Luffel and Randall²⁶ gave an example of a reservoir where saturation exponents must be measured on native-state core rather than cleaned core. The saturation exponent was first determined indirectly on the basis of logs and water saturations from core cut with an oil-based mud. The average saturation exponent was determined to be 2.6. The saturation exponent was then measured directly on native-state core, and an average value of 2.8 was obtained. In contrast, measurements on cleaned plugs gave an average value of only 1.8.

Moore²⁷ examined the effects of cleaning on the Archie saturation exponent of the Bradford Third sand, which is known to be oil-wet. Six pairs of adjacent plugs

were cut, and one from each set was extracted with toluene, making it more water-wet. The other core was unextracted, and left oil-wet. Note that cores were not preserved and probably had wettabilities that differed from their native wettability. In addition, toluene extraction may not have removed all of the organic coating on the core so the cleaned cores may not have been strongly water-wet.

The changes in the saturation exponent are shown in Table 2. In each case, extraction significantly lowered the Archie saturation exponent. Fig. 2 is a plot of the resistivity index vs. the brine saturation for one core pair. The saturation exponent, n , is the slope of the lines. It is higher for the unextracted core and appears to be constant. Moore measured the resistivity of the unextracted core only for brine saturations greater than 35%; therefore, it is possible that the saturation exponent increases rapidly at lower brine saturations, as observed by Sweeney and Jennings^{19,20} and Mungan and Moore.⁶ Moore's²⁷ and Luffel and Randall's²⁶ experiments are particularly important because they demonstrate that cleaning a core can alter the saturation exponent.

Trantham and Clampitt²⁸ measured a saturation exponent of 3.1 on plugs from the strongly oil-wet North Burbank reservoir. The plugs were cleaned and resaturated with brine and oil before measurement of the saturation exponent. Cleaning this core apparently did not affect the wettability; the plugs remained strongly oil-wet even after cleaning. Trantham and Clampitt proposed that the oil-wetness of this reservoir is a result of a coating of chamosite clay rather than the more common adsorption of surfactants from the crude. This may explain why the saturation exponent is very high even after cleaning.

The differences in the saturation exponent for native-state vs. cleaned core by Mungan and Moore,⁶ Luffel and Randall,²⁶ and Richardson *et al.*²⁹ show that the exponent should be measured on native-state or restored-state core, where alterations to the reservoir wettability are minimized. Note that it is not known whether the cores used in Refs. 6 and 26 had uniform or fractional wettability because both types of wettability are possible in reservoirs.

Fractional and Mixed-Wet Systems. Additional wettability effects can occur when a system has nonuniform wettability (either fractional or mixed), where portions of the surface are strongly water-wet, while the remainder are strongly oil-wet. Salathiel³⁰ introduced the term mixed wettability for a special type of fractional wettability in which the oil-wet surfaces form continuous paths through the larger pores. The smaller pores remain water-wet and contain no oil. Note that the main distinction between mixed and fractional wettability is that the latter does not imply either specific locations for the oil-wet and water-wet surfaces or continuous oil-wet paths.

Fractional Wettability. The only researchers who have examined the effects of fractional wettability are Schmid³¹ and Morgan and Pirson.³² Morgan and Pirson made fractionally wetted bead packs by treating a portion of the beads with an organochlorosilane solution to render them mildly oil-wet. The remainder of the beads were untreated and hence water-wet. With a variation in the proportion of oil-wet and water-wet beads, resistivity measurements could be made as the proportion of oil-

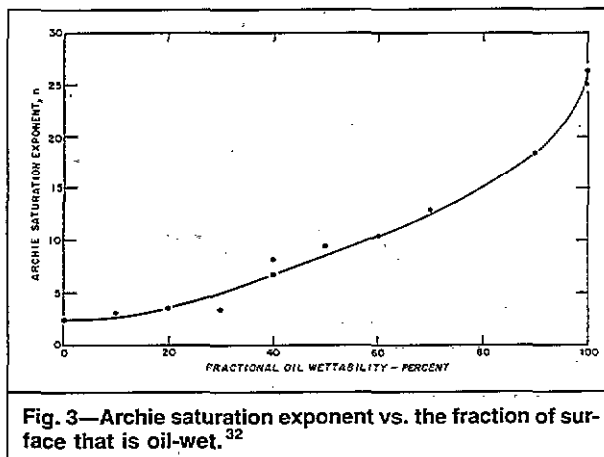


Fig. 3—Archie saturation exponent vs. the fraction of surface that is oil-wet.³²

wet surface was varied from 0 to 100%. Starting with 100% brine, the saturation was gradually reduced when oil was flowed through the pack, and the resistivity was measured. The Archie saturation exponent for each pack was found by plotting resistivity vs. the saturation. The values of n shown in Fig. 3 range from 2.5 when all of the beads were water-wet to 25 when all of the beads were oil-wet. These very high values of n possibly occur because of the smooth surfaces and homogeneous nature of the bead pack.

Schmid measured the saturation exponent in fractionally wetted sand packs with a portion of the sand grains untreated and water-wet and the remainder treated to render them oil-wet. The saturation exponent for the 100% water-wet pack was about 1.8. The resistivity index increased at a slower rate in this water-wet pack when the water saturation was less than about 25% PV. As expected, the resistivity index at any given water saturation was higher for the 100% oil-wet pack, with a saturation index of roughly 2.4. The resistivity index increased rapidly when the water saturation decreased below about 20% PV, which is similar to Mungan and Moore's⁶ and Sweeney and Jennings^{19,20} findings.

Schmid also measured the resistivity index of packings containing 25, 50, or 75% oil-wet sand grains. Unfortunately, there does not appear to be a clear trend for these packings. The 75% oil-wet pack had the same resistivity-index/saturation relationship as the 100% oil-wet pack, except there was no rapid increase in resistivity index at lower water saturations. The relationships for the 25 and 50% oil-wet packs were almost identical and were located between the completely oil-wet and completely water-wet curves.

Mixed Wettability. Unfortunately, nothing definite can be said about the electrical properties of a core with mixed wettability. In a mixed-wettability core, the oil-wet surfaces form continuous paths through the larger pores, while the smaller pores remain water-wet and contain no oil.³⁰ A mixed-wettability system can be generated in the following manner. When oil initially invaded an originally water-wet reservoir, it displaced water from the larger pores, while the smaller pores remained water-filled because of capillary forces. A mixed-wettability condition occurred if the oil deposited a layer of oil-wet organic material only on those rock surfaces that were in direct contact with the oil, but not on the brine-covered surfaces.

Oil-wet deposits would not be formed in the small water-filled pores, allowing them to remain water-wet.

Because the small pores are water-wet, the electrical behavior of mixed-wettability core will probably be different from the behavior in uniformly oil-wet systems. The Archie saturation exponent will not reach the very high values that can occur in uniformly wetted systems. Instead, it seems reasonable to expect that the electrical behavior of mixed-wettability cores will be similar to water-wet ones because the small pores and clay particles are water-wet and filled with water in both cases. As the brine saturation in a mixed-wettability core is reduced, the water in these areas will remain connected and conduct electricity. This will allow the saturation exponent to behave as it would in a water-wet core, remaining constant even at low brine saturations.

Even though the behavior of mixed-wet and water-wet cores will be similar, however, this does not imply that measurements on cleaned water-wet core are applicable to reservoir systems. Unless the reservoir is known to be strongly water-wet, the saturation exponent should be measured on native- or restored-state core. There are several reasons why core with the reservoir wettability is necessary. First, it appears that the surfactants in some crude/brine/reservoir rock systems can diffuse through a water-film, making the entire rock surface uniformly oil-wet.¹ Second, if a core has mixed wettability, the precise numerical value of the Archie saturation exponent will probably differ from that of a water-wet core because of the large oil-wet pores.

Richardson *et al.*²⁹ provided an example of the difference in resistivity for water-wet and mixed-wet systems. They measured the resistivity of native-state cores that later were shown to have mixed wettability.³⁰ The resistivity was high in the native-state cores, but gradually dropped after repeated cleaning as the cores became more water-wet. The resistivity was measured only at IWS, however, which was much higher in the mixed-wettability cores than in the cleaned water-wet ones. Richardson *et al.* present the data only after they have been corrected to a 40% saturation with Archie's law (Eq. 1). This makes it difficult to compare the resistivity measurements before and after cleaning to determine how n was affected.

Swanson³³ claimed that he saw very little change in the saturation exponent when he compared a water-wet core with the same core after it had been restored to a possibly mixed-wettability state. His experiments disagree with the measurements on native-state, mixed-wettability core discussed previously.²⁹ However, several problems with Swanson's work make it impossible to determine the actual wettability of the restored-state cores. The wettability is indeterminate because the cores were not aged for a long enough period for adsorption equilibrium to be established and because the waterflood behavior does not indicate the wettability.

Swanson first measured the waterflood and electrical resistivity behavior of clean water-wet Berea sandstone and Austin limestone cores. The cores were then driven to IWS and aged with crude oil. It is known that many cores must be aged for at least 30 to 40 days before the wettability reaches its final state.^{1,4,34-37} Unfortunately, Swanson aged the cores only between 12 and 30 days, so his cores were tested in some ill-defined, nonequilibrium state. In fact, in his discussion of the waterflood be-

havior, he stated that the waterflood behavior depended on the aging time, a clear indication that the wettability was still changing.

The cores were strongly water-wet before aging, which is demonstrated by the fact that little or no oil was produced after breakthrough during a waterflood. The waterflood behavior also demonstrated that the wettability was altered after the cores were aged because oil was produced after breakthrough in the aged cores. Unfortunately, because Swanson injected only a few PV's of brine, it is not possible to determine whether the cores had mixed wettability. On the basis of the waterflood data, the cores could be either uniformly mildly water-wet, fractionally wetted, or of mixed wettability. The primary indication of a mixed-wettability state is that very low oil saturations are reached after the injection of a very large number of PV's of brine. This is caused by the continuous oil-wetted paths through the larger pores.³⁰ In summary, no conclusions about the electrical properties of mixed-wet cores can be made from Swanson's data because the wettability of the aged cores is unknown.

Experiments in the Reservoir

Several researchers have tried to estimate the effects of wettability on resistivity in the reservoir. Pirson and Fraser⁸ and Fraser³⁸ discussed reservoirs known to be intermediate or oil-wet. Resistivity measured by the electric logs was compared with neutron logs and data on the saturation from core analysis. An Archie saturation exponent of about 3 was then determined to bring the two sets of data into agreement.

Graham³⁹ used a reverse wetting agent to examine the effects on resistivity as an originally water-wet rock was changed to oil-wet. Experiments were conducted both in cores and in situ. For the core experiments, water-wet Berea plugs were saturated with brine, oilflooded, then waterflooded to a residual oil saturation. The resistivity of the water-wet plugs was measured; then the plugs were injected with brine containing a reverse wetting agent that renders sand and clay surfaces oil-wet. The electrical resistivity of the now-oil-wet cores increased by 100 to 200% because of the redistribution of the fluids in the core. Field tests also showed an increase in resistivity after the wettability was changed to oil-wet. Graham recommended that this treatment be used when logging in regions of relatively high conductivity, where log interpretation is difficult. Oil in these regions would be revealed by the increase in resistivity after the formation was made oil-wet by the injection of a reverse wetting agent.

Formation Resistivity Factor

Another equation that Archie⁵ determined empirically relates the resistivity of the 100% brine-saturated core and the resistivity of the brine:

$$F_R = R_o / R_w, \dots\dots\dots (2)$$

where

R_o = resistivity of the brine-saturated core,

R_w = brine resistivity, and

F_R = formation resistivity factor.

Because very little work has been done on wettability effects of this parameter, it is unclear whether F_R changes

as the wettability of the core is altered. Sweeney and Jennings^{19,20} found that the formation factor was changed after the wettability was altered. Because their chemical treatment with naphthenic acids was drastic enough that other core properties such as the porosity were also altered, it is unclear whether wettability effects were demonstrated. They suggested that the naphthenic acids used to render the core oil-wet may have partially sealed off pores that had previously contributed to current flow.

Rust²¹ compared sandstone cores that were either cleaned (water-wet) or cleaned and treated with an organochlorosilane solution (mildly oil-wet). He found no significant difference in the formation factors. Mungan and Moore⁶ found no effects on the formation factor in their teflon cores. They realized, however, that this was not a conclusive test because of the uniform composition and wettability of the teflon. They went on to state, "However, because natural cores contain clays, a change in core wettability always brings about other changes, such as clay swelling and dispersion, ion exchange, effective porosity change, and surface conductance variations, and these will affect the measured values of R_o and F_R . Thus preservation of the natural core wettability is always prudent."

Conclusions

1. The Archie saturation exponent, n , is almost independent of the wettability when the brine saturation is sufficiently high that the brine is continuous.

2. Wettability effects become very important when the brine saturation is lowered. In general, essentially all the brine in a uniformly water-wet core remains continuous and electrically conducting as the brine saturation is lowered to the irreducible saturation. The Archie saturation exponent has a value of about 2 in water-wet formations and cleaned water-wet core.

3. The Archie saturation exponent can reach values of 10 or more in uniformly oil-wet core with low brine saturations. This occurs because a portion of the brine is trapped, while additional brine is isolated in dendritic fingers where it cannot contribute to the electrical conductivity. Resistivity increases because the brine cross-sectional conducting area decreases, and the lengths of the conducting paths increase.

4. Unless the reservoir is strongly water-wet, the saturation exponent should be measured on native- or restored-state cores. If a clean core is used to measure the saturation exponent and the reservoir is actually oil-wet, the interstitial water can be underestimated when logging.

5. Although no definite conclusions can be drawn about the effects of wettability on the formation factor, F_R , it is likely that the formation factor is affected by changes in wettability.

Nomenclature

- F_R = formation resistivity factor
- I_R = resistivity index
- n = saturation exponent
- R_o = formation resistivity when 100% saturated with water of resistivity R_w , $\Omega \cdot m$
- R_t = formation resistivity at a water saturation S_w , $\Omega \cdot m$
- R_w = water resistivity, $\Omega \cdot m$
- S_w = water (brine) saturation

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Wettability Literature Survey— Part 4: Effects of Wettability on Capillary Pressure

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Summary. The capillary-pressure/saturation relationship depends on the interaction of wettability, pore structure, initial saturation, and saturation history. No simple relationship exists that relates the capillary pressures determined at two different wettabilities. Therefore, the most accurate measurements are made with cores that have native reservoir wettability.

In a uniformly wetted porous medium, pore geometry effects and the extremely rough surfaces of the porous medium make the capillary pressure curve insensitive to wettability for small contact angles (less than about 50° [0.87 rad] for drainage capillary pressure curves and less than about 20° [0.35 rad] for spontaneous-imbibition capillary pressure curves). When the porous medium has fractional or mixed wettability, both the amount and distribution of the oil-wet and water-wet surfaces are important in determining the capillary pressure curve, residual saturations, and imbibition behavior. Imbibition also depends on the interaction of wettability, pore structure, initial saturation, and saturation history. Because of these interactions, there is a large range of contact angles where neither oil nor water will imbibe freely into a uniformly wetted reservoir core. In contrast, it is sometimes possible for both fluids to imbibe freely into a core with fractional or mixed wettability.

Contact Angles, Capillary Pressure, and Wettability

This paper is the fourth in a series of literature surveys covering the effects of wettability on core analysis.¹⁻⁵ Changes in the wettability of cores have been shown to affect electrical properties, capillary pressure, waterflood behavior, relative permeability, dispersion, simulated tertiary recovery, irreducible water saturation (IWS), and residual oil saturation (ROS).

When oil and water are placed together on a surface, a curved interface between the oil and water is formed, with a contact angle at the surface that can range from 0 to 180° [0 to 3.15 rad]. By convention, the contact angle, θ , is measured through the water. Generally, when θ is between 0 and 60 to 75° [0 and 1.05 to 1.31 rad], the system is defined as water-wet. When θ is between 180 and 105 to 120° [3.15 and 1.83 to 2.09 rad], the system is defined as oil-wet. In the middle range of contact angles, a system is neutrally or intermediately wet.

It can be shown that whenever an oil/water interface is curved, the pressure will abruptly increase across the interface to balance the interfacial tension (IFT) forces. This pressure jump, which is the capillary pressure, is given by Laplace's equation^{6,7}:

$$P_c \equiv p_o - p_w = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2} \right), \dots \dots \dots (1)$$

where

σ = IFT,

P_c = capillary pressure,

p_o = pressure in the oil,
 p_w = pressure in the water, and
 r_1, r_2 = radii of curvature of the interface, measured perpendicular to each other.

By convention, the capillary pressure is defined as $p_o - p_w$. Because of this definition, a radius of curvature directed into the oil is positive, while one directed into the water is negative. Depending on the curvature of the surface, the capillary pressure can be positive or negative. When the interface is flat, the capillary pressure is zero. When fluids other than oil and water are used, the capillary pressure is usually defined as

$$P_c \equiv p_{NW} - p_{WET}, \dots \dots \dots (2)$$

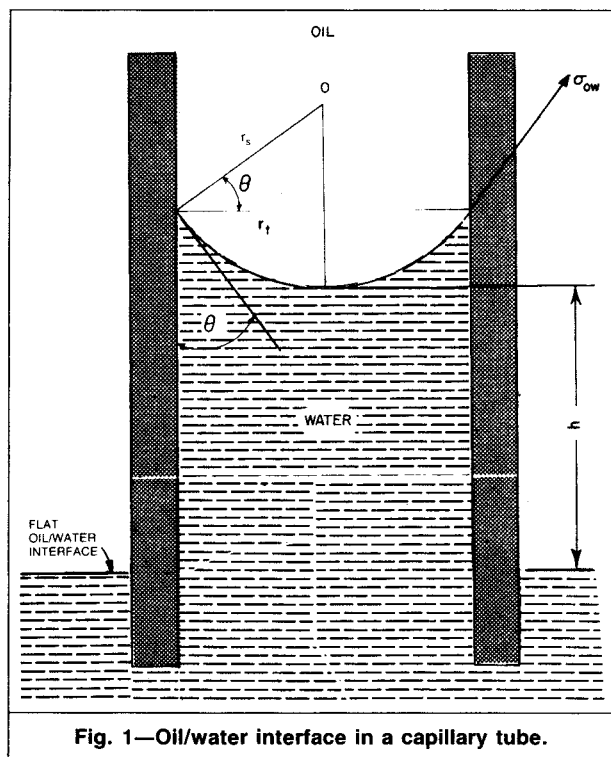
where p_{NW} is the pressure in the nonwetting fluid and p_{WET} is the pressure in the wetting fluid.

The radii of curvature of the interface, and hence the capillary pressure, are determined by local pore geometry, wettability, saturation, and saturation history. For most porous media, the equations for the interfacial curvature are much too complicated to be solved analytically, and capillary pressure must be determined experimentally. In these cases, a simple relationship between contact angle and capillary pressure cannot be derived.

One geometry where capillary pressure can be calculated as a function of geometry, wettability, and IFT is a capillary tube. Laplace's equation can be used to solve for the capillary pressure as a function of IFT, contact angle, and r_t , the radius of the tube. Fig. 1 shows an interface between two fluids, water and oil, having a con-

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tact angle of θ through the water in a capillary tube. When the capillary tube is small enough, the interface can be approximated as a portion of a sphere with radius r_s . Because the surface is spherical, both radii of curvature are also equal to r_s . Fig. 1 shows that the radius of the spherical interface is larger than the radius of the capillary tube. The relationship between the two radii is

$$\frac{r_t}{r_s} = \cos \theta$$

or

$$\frac{1}{r_s} = \frac{\cos \theta}{r_t} \quad \dots \dots \dots (3)$$

Substituting this into Eq. 1, and noting that the two radii of curvature are equal to r_s , gives an expression for the capillary pressure in terms of the tube radius and the interfacial forces:

$$P_c = \frac{2 \sigma \cos \theta}{r_t} \quad \dots \dots \dots (4)$$

To balance the upward forces caused by the IFT, the pressure in the oil above the interface is greater than the pressure in the water below. These forces are responsible for the rise (or depression) of the curved interface in a capillary tube relative to the height of a flat interface. When the surface is oil-wet, $\theta > 90^\circ$ [1.57 rad], making $\cos \theta < 0$, and the IFT force acts downward, depressing the interface in the capillary tube below the flat interface. A well-known example of capillary depression occurs with mercury/air in a glass capillary tube. Here the mercury pressure is greater than the air pressure.

On some smooth, very homogeneous surfaces, it is possible to measure a single equilibrium value for the contact angle. A range of contact angles will be measured in most systems, however, with relatively reproducible maximum and minimum values. The maximum angle is obtained by pushing the liquid over the surface, while the minimum is obtained by pushing the liquid back. These two angles are referred to as the advancing contact angle, θ_{adv} , and the receding contact angle, θ_{rec} , respectively. The difference, $\theta_{adv} - \theta_{rec}$, is the contact-angle hysteresis and can be greater than 60° [1.05 rad].⁸

Johnson and Dettre⁸ and Adamson⁶ state that there appear to be three causes of contact-angle hysteresis: surface roughness, surface heterogeneity, and surface immobility on a macromolecular scale. As discussed in more detail later, contact-angle hysteresis is one factor causing hysteresis between capillary pressures measured with increasing vs. decreasing wetting-phase saturations.

Drainage and Imbibition Capillary Pressure. There are two basic types of capillary pressure processes: drainage and imbibition. In a drainage process, the nonwetting fluid displaces the wetting fluid, while the reverse occurs for imbibition. Generally, there is hysteresis in capillary pressure as the saturation is varied, making drainage and imbibition curves different. To establish a drainage capillary pressure curve, the wetting-phase saturation is reduced from its maximum to the irreducible minimum by increasing the capillary pressure from zero to a large positive value. To develop an imbibition capillary pressure curve, the wetting-phase saturation is increased. It is important to note that two distinctly different portions of the imbibition curve can be measured. The first is the spontaneous imbibition curve, which is determined immediately after measurement of drainage capillary pressure. The capillary pressure, $P_c = p_{NW} - p_{WET}$, is decreased to zero, allowing the wetting phase to imbibe. The second portion is the forced imbibition curve, where the capillary pressure is decreased from zero to a large negative value.

Contact-angle hysteresis is one cause of capillary pressure hysteresis. During drainage, the nonwetting fluid displaces the wetting fluid from the core. The wetting fluid is being pushed back from surfaces it previously covered, so the contact angle between the fluids will be the receding angle, θ_{rec} . The advancing contact angle, θ_{adv} , is important during imbibition, when the wetting-phase saturation increases and displaces nonwetting phase from the pore walls.

An example of these three sections of the capillary pressure curve is shown in Fig. 2 for a water-wet system.⁹ Initially, when the capillary pressure is zero, all of the brine is continuous and at the same pressure. The drainage capillary pressure (Curve 1) is measured by gradually increasing the capillary pressure from zero to a large positive value, which reduces the saturation of the wetting phase (water). As the saturation is decreased, portions of the wetting phase become disconnected from the bulk wetting phase. Eventually, when the externally applied capillary pressure is sufficiently high, all of the wetting phase remaining in the core will be disconnected and the capillary pressure curve will be almost vertical. This saturation, where hydraulic continuity of the wetting phase is lost, is the irreducible wetting-phase saturation.^{7,10}

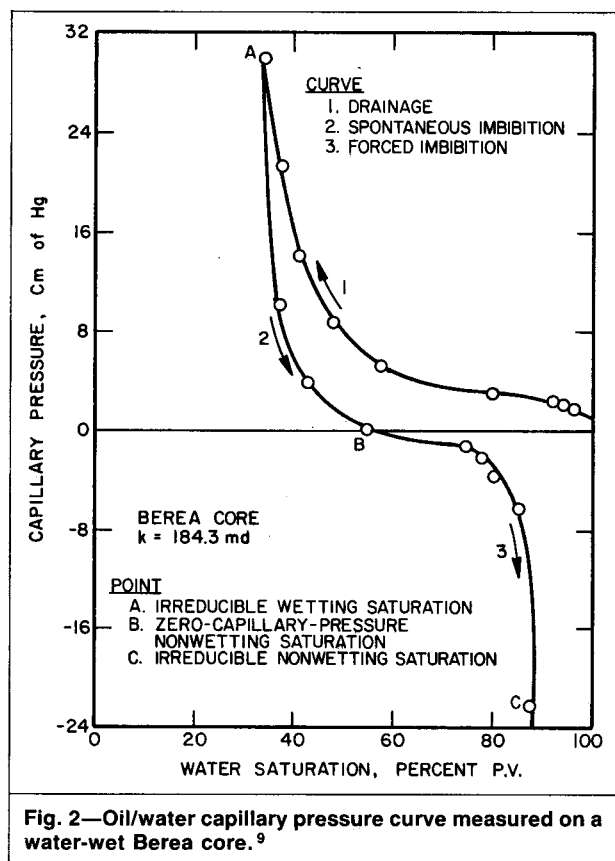


Fig. 2—Oil/water capillary pressure curve measured on a water-wet Berea core.⁹

Curve 2 of Fig. 2 is the spontaneous imbibition curve, determined after the drainage capillary pressure curve is measured. The capillary pressure, initially at a large positive value, is gradually decreased to zero, allowing the wetting phase (water) to imbibe. The nonwetting residual saturation reached when $P_c = 0$ will be referred to as the zero-capillary-pressure nonwetting saturation. In general, some of the oil (nonwetting phase) is still connected when the capillary pressure is zero, so the nonwetting-phase residual saturation defined in this fashion is not irreducible.

Curve 3 of Fig. 2 is the forced imbibition curve, where the capillary pressure, $p_o - p_w$, is decreased from zero to a large negative value. When the capillary pressure is negative, the pressure in the wetting phase (water) is greater than the pressure in the nonwetting phase (oil), forcing water into the core. (Note that the fact that the water pressure is greater than the oil pressure does not imply that the oil is the wetting fluid at these saturations. If the core were a bundle of cylindrical capillary tubes, then negative capillary pressures would be possible only if the core were oil-wet. However, the interaction of pore structure and wettability allows negative capillary pressures even for strongly water-wet cores.¹¹) Much of the oil (the nonwetting phase) is still connected at the end of the spontaneous imbibition curve when the capillary pressure is zero because additional oil is produced as the capillary pressure becomes negative. The oil saturation decreases, and the oil gradually disconnects as the capillary pressure becomes increasingly negative until the capillary pressure curve is almost vertical. This saturation, where hydraulic continuity of the nonwetting phase is lost, will be referred to as the irreducible nonwetting-phase satu-

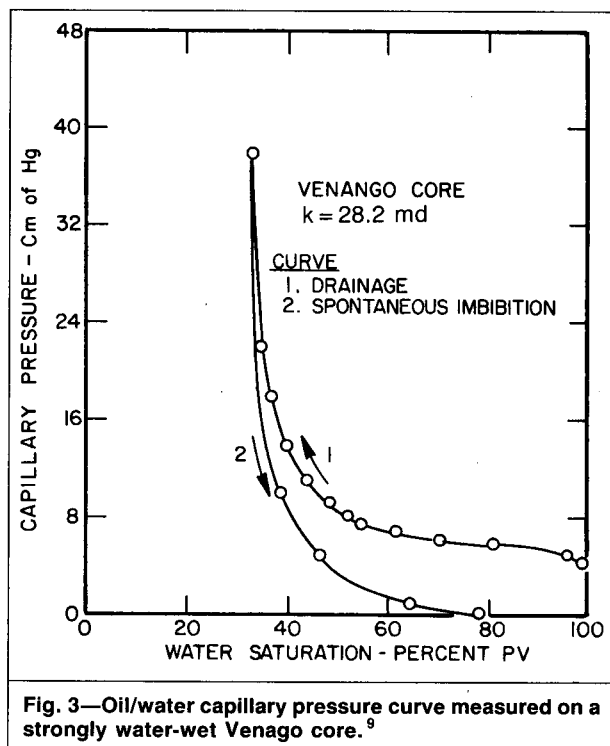


Fig. 3—Oil/water capillary pressure curve measured on a strongly water-wet Venago core.⁹

ration. In general, different residual nonwetting-phase saturations will be measured after the spontaneous and forced imbibition curves unless the core is very strongly wetted.^{7,12}

Capillary Pressure Curves in Strongly Wetted Systems

The capillary-pressure/saturation relationship is a function of wettability, pore structure, and saturation history. Before discussing how changes in wettability affect capillary pressure, we will examine capillary pressure curves measured on strongly water-wet and strongly oil-wet systems. This discussion will be based on early work at Pennsylvania State U.^{9,13-17} Figs. 2 through 5, taken from Killins *et al.*,⁹ show capillary pressure curves measured on strongly wetted systems using a porous-plate apparatus. Figs. 2 and 3 are for strongly water-wet plugs, while Figs. 4 and 5 are for strongly oil-wet ones. All of the plugs were cleaned with toluene, dried, then saturated with their wetting fluid (water for Figs. 2 and 3, oil for Figs. 4 and 5). Capillary pressures were measured with a refined oil and brine.

Fig. 2 is the capillary pressure measured on a water-wet Berea plug, while Fig. 3 is for a strongly water-wet Venago plug. The strong water wetness of the plug shown in Fig. 2 causes the areas under the drainage (Curve 1) and forced imbibition (Curve 3) curves to differ significantly. Because of the favorable free energy change, little or no work must be done during imbibition, when the preferentially wetting fluid (water) displaces the nonwetting fluid (oil). Conversely, a great deal of work is required during drainage when the nonwetting fluid displaces the wetting one from the core. It can be shown

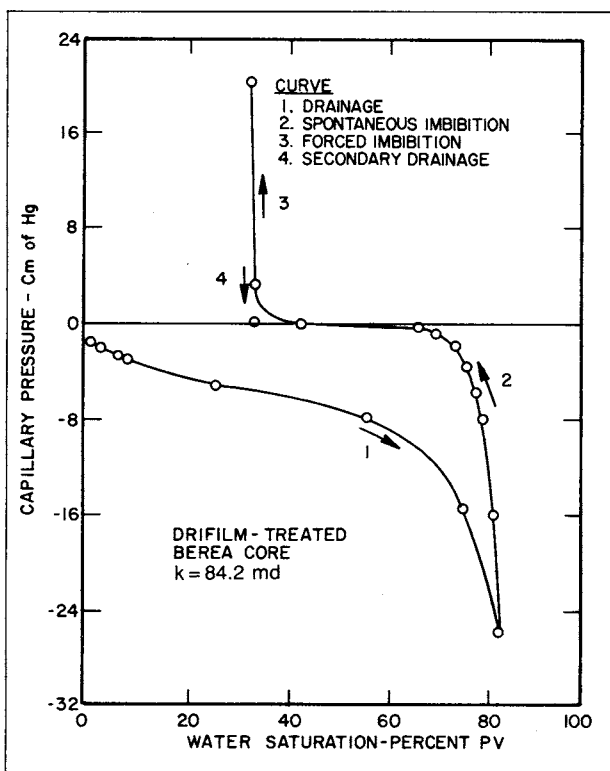


Fig. 4—Oil/water capillary pressure curve measured on an oil-wet Berea core treated with Drifilm.⁹

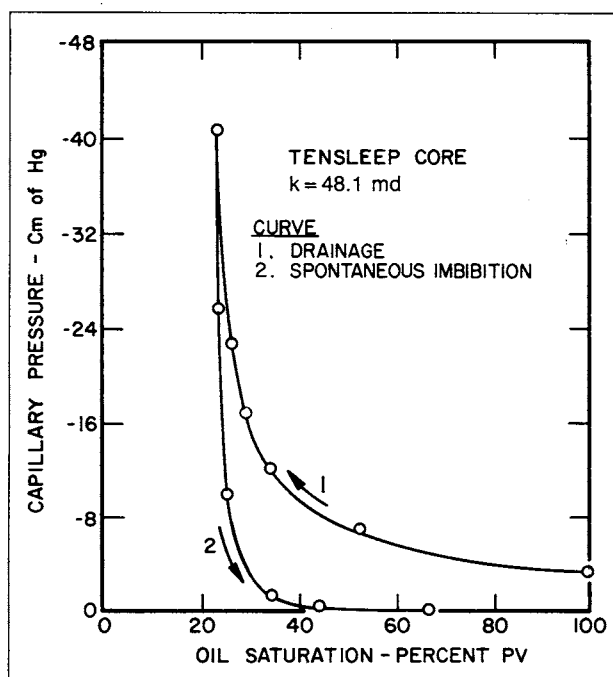


Fig. 5—Oil/water capillary pressure curve measured on a strongly oil-wet Tensleep sandstone core. Note that the curves are plotted vs. oil saturation and with negative capillary pressures upward.⁹

that the work required for one fluid to displace the other from the core is related to the area under the capillary pressure curve. For oil displacing water (drainage curve in a water-wet core, Curve 1), the external work required is^{18,19}

$$\Delta W_{\text{ext}} = -\phi V_b \int_{S_{w1}}^{S_{w2}} P_c dS_w, \dots\dots\dots (5)$$

where

- V_b = bulk volume of the core,
- ϕ = porosity, and
- S_w = water saturation.

Similarly, the work required for water to displace oil (forced imbibition curve for a water-wet core) is

$$\Delta W_{\text{ext}} = \phi V_b \int_{S_{o1}}^{S_{o2}} P_c dS_o, \dots\dots\dots (6)$$

The area under the drainage capillary pressure curve in Figs. 2 and 3 is relatively large because a great deal of work is necessary for the oil to displace the water. The Venago core is very strongly water-wet because a great deal of the water imbibes back spontaneously and the residual oil saturation is approached at zero capillary pressure. The water saturation after spontaneous imbibition is almost 80% PV. The Berea core shown in Fig. 2 is less strongly water-wet. After spontaneous imbibition, the water saturation is only about 55% PV, and additional water can be forced into the core (Curve 3, Fig. 2). The

area under the imbibition curve (Eq. 6), however, is much smaller than the area under the drainage curve (Eq. 5), so more work is necessary for oil to displace water than for the reverse displacement. This shows the degree of water wetness.

Figs. 4 and 5 show the capillary pressure measured in strongly oil-wet systems. The Berea plug shown in Fig. 4 was treated with DrifilmTM, an organochlorosilane, to render it strongly oil-wet.¹ The Tensleep sandstone plug shown in Fig. 5 was naturally strongly oil-wet even after it was cleaned with toluene and dried. The plugs were first saturated with oil, then the drainage capillary pressure curve (Curve 1 in Figs. 4 and 5) was measured by increasing the capillary pressure, $p_o - p_w$, to a large, negative value. Because oil is the wetting fluid, a large amount of work is necessary to force water into the core, as shown by the large area under Curve 1 (see Eq. 6).

When oil is the strongly wetting fluid, the roles of oil and water are reversed from the strongly water-wet case. To demonstrate this, Fig. 5 for the oil-wet Tensleep plug has been inverted from a normal capillary pressure plot. The curve is plotted vs. oil saturation and with negative capillary pressure plotted upward. Note the very strong resemblance to Fig. 3 for the water-wet Venago plug. Similarly, if Fig. 4 for the oil-wet Berea plug were inverted, it would resemble the capillary pressure curve shown in Fig. 2 for the water-wet Berea plug.

Curve 2 in Figs. 4 and 5 is the spontaneous imbibition curve, measured as the capillary pressure is reduced to zero. Because oil is the wetting fluid, it imbibes spontaneously, just as water imbibed in the water-wet plugs. Curve 3 in Fig. 4 is the forced imbibition curve. The capillary pressure, $p_o - p_w$, is increased to a large positive

value, forcing additional oil into the core. Again, the areas under the capillary pressure curves show that the work required for this displacement is much smaller than the work for the reverse displacement, where the nonwetting fluid displaces the wetting fluid from the core. Curve 4 in Fig. 4 shows that no water is imbibed as the capillary pressure is reduced to zero.

As the rock/oil/brine system becomes more neutrally wetted, the transition zone and the area under the drainage capillary pressure curve are reduced. This occurs because less work is necessary for drainage as the preference of the rock surface for the wetting phase decreases. Consider a weakly water-wet system compared with a strongly water-wet one; more water would be displaced by oil at any given capillary pressure, giving a lower water saturation. Another way of stating this is that at any given capillary pressure, the nonwetting fluid (oil) would be able to enter smaller and smaller pores as the water wetness of the system was reduced. In addition, the amount of wetting fluid (water) imbibed during the spontaneous imbibition curve would also decrease as the system becomes more neutrally wet because the driving force is reduced. The behavior in an oil-wet system is analogous. As the system moves from strongly oil-wet to neutrally wet, the area under the drainage capillary pressure curve would decrease, as would the amount of spontaneous oil imbibition.

Finally, drainage capillary pressure curves can be measured even if the contact angle is 90° [1.57 rad]. In general, external work will still be necessary for one fluid to displace the other, causing a finite area under the capillary pressure curve. This disagrees with the capillary tube model. Experiments on neutrally wetted systems are discussed below.

Theoretical Relationships for the Effects of Wettability on Capillary Pressure

To obtain the most accurate capillary pressure curve, measurements are made with native- or restored-state core using crude oil and brine. It is often more convenient, however, to measure capillary pressure with a different pair of fluids, such as air/brine or air/mercury, in cleaned cores. These measurements are subsequently used to obtain the oil/brine capillary pressure curve, although obviously with a different IFT, contact angle, and wettability. Unfortunately, because of the complex geometry of the core, we can only approximate the factor used to convert between different fluid pairs. Additionally, the measured residual saturations may differ.²⁰ Craig²¹ strongly recommends that the air/brine or air/mercury curves be used only if the formation is known to be strongly water-wet. In spite of this limitation, several simple models have been proposed that allow the conversion of the capillary pressure curve measured with one set of fluids to the curve for a different set. Experiments demonstrate that the most accurate conversion factor for drainage in a uniformly wetted core, with contact angles roughly between 0 and 50° [0 and 0.87 rad], neglects the contact angle. The reasons for this will be discussed.

The most common method to approximate the oil/brine capillary pressure with another pair of fluids assumes that a core behaves as a bundle of capillary tubes.²² For the same capillary tube and two fluid pairs, such as oil/brine and air/brine, Eq. 4 can be solved to give

$$\frac{(P_c/\sigma)_1}{(P_c/\sigma)_2} = \frac{\cos \theta_1}{\cos \theta_2} \quad (7)$$

This equation neglects the departure of pore geometry from a cylindrical tube. As discussed in the next section, experiments show that Eq. 7 is valid only for capillary tubes and is a poor approximation for porous media.

Various authors^{23,24} have suggested that a better correlation can be obtained by use of

$$P_c = \frac{2\sigma}{r_t} f(\theta) \quad (8)$$

The conversion between capillary pressures measured with two different fluid pairs then becomes

$$\frac{(P_c/\sigma)_1}{(P_c/\sigma)_2} = \frac{f(\theta_1)}{f(\theta_2)} \quad (9)$$

The experiments discussed in the next section show that this equation is valid until the contact angle approaches 90° [1.57 rad]. Note that because no uniform $f(\theta)$ function exists, there is a different expression for each type of reservoir rock,^{25,26} reducing the usefulness of the correlation.

Amyx *et al.*²⁵ discuss a simple correlation that appears to give reasonable results for drainage capillary pressures in uniformly wetted cores when the contact angle is less than about 50° [0.87 rad]. If it is assumed that the radii of curvature are unique functions of the wetting-phase saturation for a given displacement process (either imbibition or drainage), then Laplace's equation (Eq. 1) can be rewritten expressing the capillary pressure as a function of saturation:

$$P_c/\sigma = g(S_w) \quad (10)$$

The correlation between two fluid pairs is then

$$(P_c/\sigma)_1 = (P_c/\sigma)_2 = g(S_w)$$

or

$$\frac{(P_c)_1}{(P_c)_2} = \frac{\sigma_1}{\sigma_2} \quad (11)$$

This correlation, which neglects contact angle, appears to be valid experimentally because the rough surfaces of the pores make the effective contact angle zero. (See the section on surface roughness.)

Leverett J Function. It is often necessary to compare capillary pressure curves measured on different cores from the same reservoir. Because capillary pressure is affected by both permeability and porosity, it is necessary to correct for these effects before a proper comparison can be made. This is generally done with the empirical Leverett J function¹⁸:

$$J(S_w) = \frac{P_c}{\sigma} \left(\frac{k}{\phi} \right)^{1/2} \quad (12)$$

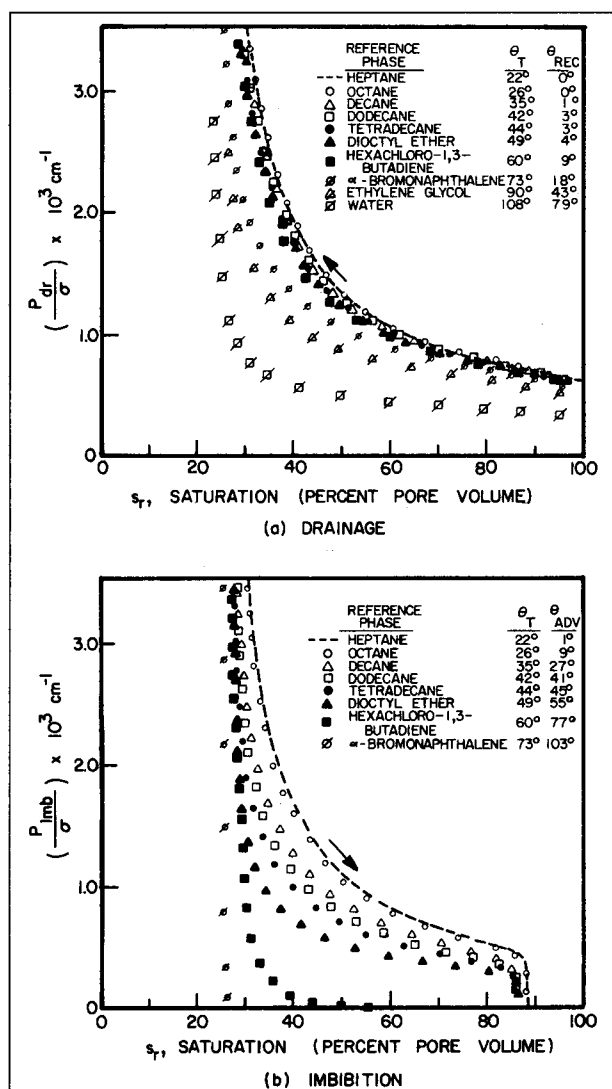


Fig. 6—Effect of contact angle on drainage and imbibition capillary pressures, air/liquid in teflon cores. S_r is the reference phase (liquid) saturation and θ_T is the contact angle measured on a flat plate. θ_{rec} and θ_{adv} are the receding and advancing contact angles measured with a liquid drop on roughened teflon surfaces.²⁹

where k is the absolute permeability and ϕ is the porosity.

In many cases, all of the capillary pressure data from a formation will be reduced to a single curve when the Leverett J function is plotted vs. the saturation. Note that some authors alter the expression for the J function by including the cosine of the contact angle²⁷:

$$J(S_w) = \frac{P_c}{\sigma \cos \theta} \left(\frac{k}{\phi} \right)^{1/2} \dots \dots \dots (13)$$

As will be discussed in the next section on experimental results, the $\cos \theta$ relationship is not valid for the effects of wettability on capillary pressure in reservoir cores. Hence the original J function without the $\cos \theta$ term should be used. Actually, as long as all of the measurements are made with reservoir fluids on cores with the reservoir wettability, the $\cos \theta$ term will act as a constant multiplier and not affect the results. Problems arise when different fluids are used or the core is cleaned.

Experimental Wettability Effects

In this section, the effects of wettability on capillary pressure will be studied using cores with two different types of surfaces: uniform and heterogeneous. In the first set of experiments with uniform wettability, the wettability of the entire core is varied from water-wet to oil-wet. At any given wettability, the wettability of the entire surface is kept as uniform as possible. Additional wettability effects will occur if the core has fractional or mixed wettability, where some of the rock surfaces are strongly water-wet but the remainder are strongly oil-wet. In this second set of experiments, the effects of wettability are studied by varying the proportion of the surfaces that are water-wet vs. oil-wet.

Drainage Capillary Pressure. Morrow and Mungan²⁸ and Morrow²⁹ examined the effects of wettability on capillary pressures using sintered porous polytetrafluoroethylene (teflon) cores. Air and an assortment of pure fluids without surface-active agents were used to vary the contact angle and wettability while keeping the geometry fixed. The contact angles, θ_T , were measured on a flat, smooth teflon surface, while drainage and imbibition capillary pressures were measured by the porous-plate method. The advantage of using a teflon core is that it is chemically inert and has uniform wettability. This allows wettability effects to be studied without worrying about heterogeneous wettability or wettability alteration. Once the fluids are chosen, the contact angle in the core will have a fixed, known value when the contact line is on a smooth surface. As noted above, however, most of the contact lines will lie along sharp edges in the core where the contact angle can have a range of values.

Typical results taken from Morrow and Mungan²⁸ and Morrow²⁹ for drainage and imbibition capillary pressure are shown in Figs. 6a and 6b, respectively. Probably the most important result shown in Fig. 6a is that the drainage capillary pressure curves are almost independent of wettability for contact angles (θ_T) of 50° [0.87 rad] and less. When the contact angle was less than 22° [0.38 rad], they found no measurable effect of contact angle (or wettability). Although they are not shown in the figure, the drainage capillary pressure curves for pentane ($\theta_T=0^\circ$) and hexane ($\theta_T=7^\circ$ [0.12 rad]) were identical to the curve for heptane ($\theta_T=22^\circ$ [0.38 rad]). Between $\theta_T=22^\circ$ [0.38 rad] and $\theta_T=50^\circ$ [0.87 rad], there is a slight influence of wettability on capillary pressure but much smaller than the effect predicted by Eq. 7 using $\cos \theta_T$.

Morrow and Mungan used Eq. 9 to show the effects of wettability on capillary pressure. All of the capillary pressure curves were compared using the zero contact angle case as a reference. Letting

$$f(\theta_2) = f(0) = 1, \dots \dots \dots (14)$$

Eq. 9 becomes

$$\frac{(P_c/\sigma)_1}{(P_c/\sigma)_{\theta=0}} = f(\theta_1), \dots \dots \dots (15)$$

where pentane ($\theta=0^\circ$, $\cos \theta=1$) is the reference capillary pressure curve.

Morrow and Mungan demonstrated that the capillary tube model is invalid by comparing the true contact angle, θ_T , measured on a smooth, flat surface with an apparent contact angle, θ_a , calculated from Eq. 15:

$$\cos \theta_a \equiv f(\theta_T)$$

or

$$\theta_a = \cos^{-1} [f(\theta_T)] \quad (16)$$

If the capillary tube model (Eq. 7) is valid, then the calculated θ_a would be equal to the contact angle measured on a flat plate, θ_T . The greater the difference between the true and apparent contact angles, the worse the capillary tube model is for representing a porous medium.

Morrow and Mungan used Eq. 16 to calculate the apparent contact angles, θ_a , during drainage and imbibition in their air/liquid/teflon systems. In a separate set of experiments, Morrow³⁰ measured advancing and receding contact angles using the same fluid pairs on roughened teflon surfaces. A close correspondence was found between the apparent contact angle computed during drainage, θ_a , and the receding contact angle on a rough surface, θ_{rec} .

Fig. 6a contains a comparison between θ_T and θ_{rec} (θ_a and θ_{rec} are almost identical). The error that occurs when a cosine relationship (Eq. 7) is assumed is clearly shown. The apparent contact angle in the drainage case is almost zero when the true contact angle is slightly less than 50° [0.87 rad]. When θ_T is increased beyond 50° [0.87 rad], the effects of wettability become increasingly apparent as the capillary pressure curves start to develop a sharp knee (see Fig. 6a). The apparent contact angle, θ_a , increases, although at a slower rate than does θ_T . Note that even when θ_T is 108° [1.88 rad] for water/air, θ_{rec} is still only 79° [1.38 rad]. Because θ_T is greater than 90° [1.57 rad], this capillary pressure curve is actually a forced imbibition curve.

As θ_T approaches 90° [1.57 rad], it becomes less useful to model the effects of wettability with an apparent contact angle in a capillary tube model. The best choice of θ_a to satisfy Eq. 16 becomes a function of both contact angle and saturation. For example, Morrow²⁹ found that when $\theta_T = 90^\circ$ [1.57 rad], the calculated θ_a varied from 37 to 43° [0.65 to 0.75 rad] as the saturation was varied. Wide variations in the apparent contact angle as the saturation is varied have also been reported when comparing different fluid pairs in reservoir cores^{31,32} (which possibly had nonuniform wettability). Unfortunately, the wettability conditions are unknown for these experiments.

A great deal of the early work on wettability effects was done at Pennsylvania State U. Their results on strongly wetted systems have already been discussed in a previous section.^{9,13-17} In addition to this work, they also investigated the effects of wettability on capillary pressure for less strongly wetted cores.³³⁻³⁵ Initially water-wet artificial cores were treated with different concentrations of organochlorosilanes in an attempt to achieve different strengths of oil wetness. Unfortunately, there was no good measure of the wettability of the treated cores. The wettability of the treated core varies, depending on such variables as the organochlorosilane used, the treat-

ment time, the time elapsed since the surface was treated, and the brine pH.^{1,36} Because it is impossible to obtain more than a rough estimate of the treated wettability, this work will not be reviewed here.

Experiments on the effects of wettability on capillary pressure for uniformly wetted systems were also made by others.³⁷⁻⁴⁰ Morrow *et al.*³⁸ measured capillary pressure using brine and refined oil in close-sized packings of powdered dolomite. The wettability was controlled by addition of different concentrations of octanoic acid (a carboxylic acid). They compared the contact angle measured on a flat surface with the apparent contact angle computed from the drainage capillary pressure data. Their results also showed that the apparent contact angle is much less than the true contact angle, which agrees with the experiments of Morrow and Mungan²⁸ and Morrow.²⁹

Mercury Drainage Capillary Pressure. Previously, the experiments of Morrow and Mungan were presented to show that drainage capillary pressure is not sensitive to the contact angle when it is less than about 50° [0.87 rad]. In this section, we will show that this is consistent with the experimental data for mercury capillary pressures. Purcell¹¹ introduced the mercury injection method for determining drainage capillary pressure, which forces mercury into an evacuated core. The contact angle through the mercury is about 140° [2.44 rad] (or 40° [0.7 rad] through the vacuum), making mercury the nonwetting fluid. Once the mercury capillary pressure curve is determined, it must be converted to an equivalent oil/brine or air/water capillary pressure curve. To do so, Purcell modeled the core as a bundle of capillary tubes and used Eq. 7 to compare mercury/vacuum capillary pressures with air/water capillary pressures determined in reservoir cores by the porous-plate method. The contact angle through the water was 0° for air/water, indicating that water was the wetting phase. Purcell stated that he obtained a fairly good correlation between the two sets of capillary pressures. Amyx *et al.*,²⁵ however, pointed out that a better correlation of Purcell's data was generally obtained from Eq. 11, where the contact angle is neglected.

Brown²⁶ compared mercury/vacuum with air/water capillary pressures determined by the porous-plate method, and calculated the empirical scaling factor that brought the two capillary pressures into agreement.

$$F \equiv \frac{(P_c)_{Hg}}{(P_c)_{aw}} \quad (17)$$

An examination of his data shows that the scaling factor based on Eq. 11,

$$F = \frac{\sigma_{Hg}}{\sigma_{aw}} = 6.9, \quad (18)$$

which neglects the contact angle, gave a better correlation than the factor obtained by rearranging Eq. 7,

$$F = \frac{\sigma_{Hg} \cos \theta_{Hg}}{\sigma_{aw} \cos \theta_{aw}} = 5.25, \quad (19)$$

which models the core as a bundle of capillary tubes. However, Brown found that the optimum scaling factor was dependent on the lithology of the core. Average values were about 6.4 for limestone and 7.2 for sandstone. Note that there was a fair amount of scatter in the data for all cores, with experimental values of the scaling factor ranging from 5.4 to 8.3.

Dumore and Schols⁴¹ compared drainage capillary pressure measurements in Bentheim sandstone plugs using different fluid pairs: mercury/air, air/water, and several refined-hydrocarbons/water. The plugs were cleaned, then fired at 930°F [500°C] for at least 12 hours to render them strongly water-wet. They found very good agreement between the different capillary pressure curves using Eq. 11, which neglects the contact angle. They suggested that the apparent contact angle was zero because of the rough nature of the pore surfaces.

More recently, Swanson⁴² compared mercury/vacuum capillary pressure measurements with porous-plate oil/brine measurements in a strongly water-wet sandstone plug. He obtained good agreement between the two measurements with Eq. 12 for the Leverett J function, which neglects the contact angle. On the other hand, Omoregie⁴³ compared mercury/vacuum capillary pressure measurements with air/brine and air/oil centrifugal measurements. He used Eq. 13 for the Leverett J function, which includes $\cos \theta$, and obtained good agreement between the three sets of measurements. The contact angle was assumed to be 140° [2.44 rad] through the mercury and 0° through the brine or oil. The reason for this discrepancy is unknown.

Another use of mercury drainage capillary pressure is the calculation of pore-throat-size distribution.^{44,45} The system is modeled as a bundle of capillary tubes, and Eq. 4 is used to calculate the size of the pore throat invaded at each capillary pressure. The contact angle generally used in Eq. 4 is 140° [2.44 rad], based on contact angles measured on flat surfaces by Ritter and Drake.⁴⁵ They measured the contact angle on the smooth surface of a large variety of materials, obtaining values ranging from 135 to 142° [2.36 to 2.48 rad], with an average value of about 140° [2.44 rad]. However, we are not aware of any experimental verification of this value in porous media. In addition to contact angle measurements on flat surfaces, the only other measurements have used circular capillary tubes drilled into the test material.^{46,47} These experiments are not applicable to porous materials because they neglect the effects of roughness and pore geometry.

Good and Mikhail⁴⁸ examined the best choice of contact angle and concluded that the contact angle should be neglected ($\theta = 180^\circ$ [3.14 rad] through the mercury, so $\cos \theta = 1$). Good and Mikhail found experimental evidence for this conclusion in the work of De Witt and Scholten,⁴⁹ who compared pore-throat-size distributions calculated by mercury injection and nitrogen capillary condensation. Good and Mikhail pointed out that the best match between the two distributions was generally obtained by setting $\theta = 180^\circ$ [3.14 rad]. They stated that this was because of the pore structure and the rough nature of the pore walls.

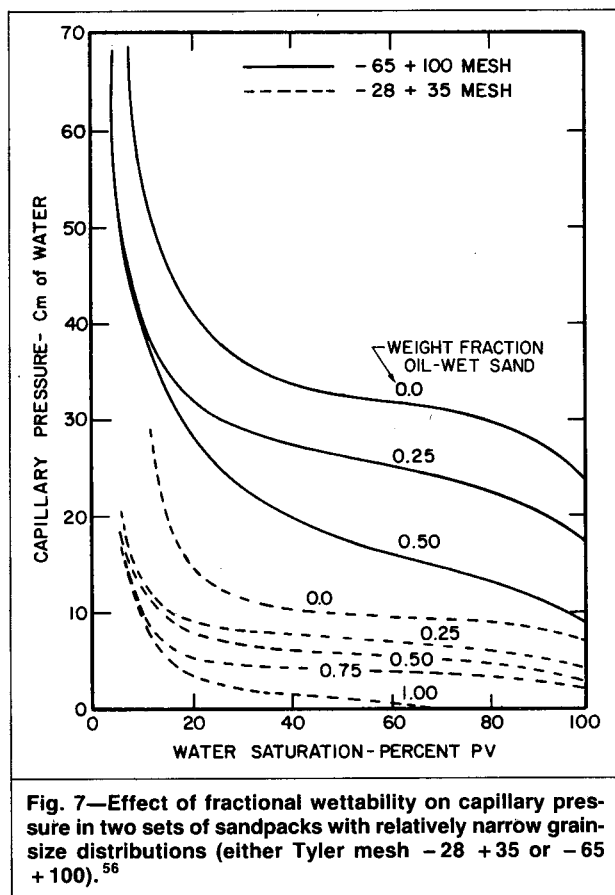
Imbibition Capillary Pressure. Morrow and Mungan²⁸ and Morrow²⁹ also measured spontaneous imbibition capillary pressure curves with teflon cores, air, and pure

fluids. After drainage capillary pressure measurements, spontaneous imbibition curves were measured as the capillary pressure was decreased from a large positive value to zero. The results are shown in Fig. 6b. There was no measurable effect on the spontaneous imbibition capillary pressure curves as the contact angle, θ_T , was varied between 0 and 22° [0 and 0.38 rad]. Although they are not shown on the figure, the imbibition capillary pressure curves of pentane ($\theta_T = 0^\circ$) and hexane ($\theta_T = 7^\circ$ [0.12 rad]) were identical to the curve for heptane $\theta_T = 22^\circ$ [0.38 rad]. In contrast to the drainage data, however, the imbibition results were sensitive to the contact angle when θ_T was larger than 22° [0.38 rad]. The insensitivity of the imbibition capillary pressure curve to contact angle when θ_T is less than 22° [0.38 rad] does not invalidate the U.S. Bureau of Mines (USBM) wettability measurement. Morrow and Mungan's data are based on spontaneous imbibition curves measured as the capillary pressure is decreased from a large positive value to zero. The USBM method uses the forced imbibition curve measured when the capillary pressure is decreased from zero to a large negative value, where the pressure in the wetting phase is greater than the pressure in the nonwetting phase (Curve 3 of Fig. 2).

Eq. 19 was used to calculate the apparent contact angles, θ_a , during the imbibition measurements. A close correspondence was found between θ_a and the advancing contact angle, θ_{adv} , measured with the same fluids on a rough teflon surface.³⁰ Fig. 6b contains a comparison between θ_T and θ_{adv} (θ_a and θ_{adv} are almost identical). As for the drainage case, the apparent contact angle, θ_a , was quite different from the true contact angle, θ_T . As θ_T is increased, θ_{adv} and θ_a first underestimate and then overestimate θ_T .

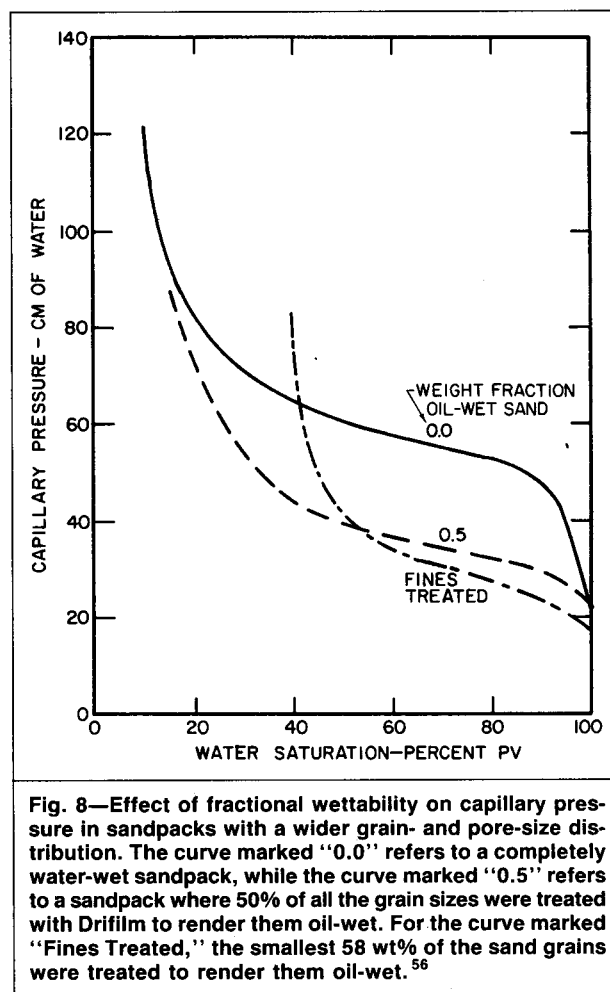
In imbibition, Morrow and Mungan found that the capillary pressure curve was insensitive to contact angle when θ_T was less than 22° [0.38 rad], while the drainage curve was insensitive when θ_T was less than 50° [0.87 rad]. This is because of the different behavior of the advancing and receding contact angles measured on a rough surface.³⁰ The advancing contact angle, important during imbibition, was insensitive for $\theta_T < 22^\circ$ [0.38 rad]. The receding contact angle, important during drainage, was insensitive for θ_T less than about 50° [0.87 rad]. Further details can be found in Morrow^{29,30} and Morrow and McCaffery.⁵⁰

Morrow and Mungan also measured two forced imbibition curves, where the capillary pressure was decreased to a large negative value. Data for the fluid pairs ethylene-glycol/air ($\theta_T = 90^\circ$ [1.57 rad]) and water/air ($\theta_T = 108^\circ$ [1.88 rad]) are shown in Fig. 6a. The ethylene-glycol/air curve is actually neither an imbibition nor a drainage curve because the system has neutral wettability with no wetting preference for either fluid. In the water/air/teflon system, the air is the wetting fluid because the contact angle through the water is 108° [1.88 rad]. This curve is actually a forced imbibition curve because the wetting fluid displaces the nonwetting fluid while the capillary pressure, $P_c = p_{NW} - p_{WET}$, decreases to a large negative value. Note that there is still a substantial area under the capillary pressure curve even though the wetting fluid is imbibing. The wetting preference of the teflon core for air is small enough that work must be done to force air into the core.



The capillary pressure and contact-angle measurements by Morrow and Mungan,²⁸ Morrow,^{29,30} and Morrow and McCaffery⁵⁰ found that the receding contact angle measured on a rough teflon surface characterizes the wettability during drainage capillary pressure measurements in teflon cores. Similarly, the advancing contact angle characterizes imbibition capillary pressure measurements. This indicates that departure of the pore geometry from a bundle of capillary tubes had little effect on the interaction of pore geometry and wettability to determine capillary pressure. Morrow and McCaffery⁵⁰ point out, however, that this result should be regarded as fortuitous and may not extend to capillary pressure measurements in reservoir rock. Note also that these results do not imply that the porous medium can be modeled as a bundle of capillary tubes. Imbibition results, discussed in more detail below, show that the bundle-of-capillary-tubes model is not valid for imbibition in teflon cores.⁵⁰⁻⁵²

Kruyer⁵³ developed a model for the effects of contact angle on imbibition capillary pressure in packings of uniform spheres and applied this model to mercury imbibition capillary pressure. He found experimentally that the best fit for glass spheres and smooth metal balls was 150° [2.62 rad] through the mercury. However, some of the metal spheres were accidentally corroded (roughened). The best fit for the apparent contact angle through the mercury for these rough spheres was 180° [3.14 rad]. Note that Kruyer did not model his system as a capillary tube



bundle, so his results should not be compared directly with the apparent contact angles calculated by Morrow and Mungan. The important result of his work is that the apparent contact angle for smooth and rough sphere packs differs.

Fractional and Mixed-Wet Systems. In the experiments discussed previously, the wettability of the core was varied while the wettability of the entire surface was kept as uniform as possible. For example, all of the rock surface in a neutrally wet core should have little preference for oil or water. Additional wettability effects will occur when the system has nonuniform wettability (either fractional or mixed), where portions of the surface are strongly water-wet while the remainder are strongly oil-wet.^{1,54} Salathiel⁵⁵ introduced the term "mixed" wettability for a special type of fractional wettability in which the oil-wet surfaces form continuous paths through the larger pores. The smaller pores remain water-wet, containing no oil. Note that the main distinction between mixed and fractional wettability is that the latter does not imply either specific locations for the oil-wet and water-wet surfaces or continuous oil-wet paths.

Fatt and Klikoff⁵⁶ used the porous-plate method to measure capillary pressure of fractionally wetted sandpacks. The fractionally wetted sandpacks were formed by mixing treated and untreated sand grains together. The untreated sand grains were strongly water-wet. The re-

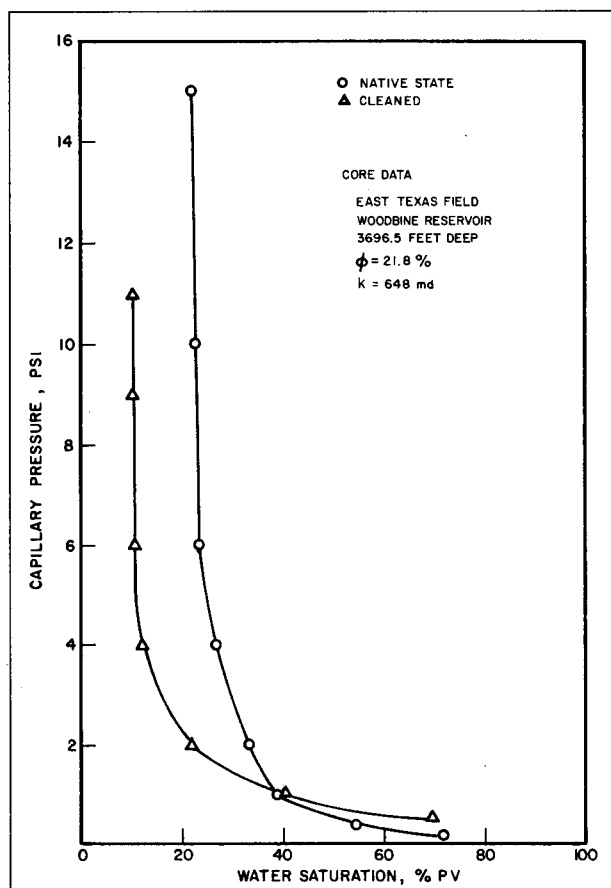


Fig. 9—Comparison of capillary pressure curves measured on a single core in the native and cleaned states. The core is mixed-wet in the native state, and water-wet after cleaning.⁶⁰

maining sand grains were treated with Drifilm to render them oil-wet. Note that during mixing some Drifilm may have been transferred to some of the water-wet sand grains, probably giving them a nonzero contact angle.⁵⁶ The sandpacks were placed in the porous-plate apparatus, then saturated with water. Kerosene was used to measure the capillary pressure for oil displacing water. Fig. 7 shows the capillary pressure curves measured on two sets of sandpacks with relatively narrow grain size distributions (either Tyler mesh $-28 + 35$ or $-65 + 100$). As the fraction of oil-wet sand increases, the area under the curve decreases, indicating that it is easier for the oil to displace the water. Because of the relatively narrow grain- and pore-size distribution, all the curves are fairly flat until IWS is reached. Similar results were reported by Talash and Crawford.^{57,58}

Fig. 8 shows the capillary pressure curve measured on a fractionally wet sandpack with a much wider grain- and pore-size distribution.⁵⁶ Again, the area under the curve decreases when the fraction of oil-wet grains is increased from 0 to 50%. Fatt and Klikoff also demonstrated the importance of the location of the oil-wet vs. water-wet surfaces. The curve marked "Fines Treated" in Fig. 8 shows the capillary pressure curve when only the smallest-sized sand grains were treated with Drifilm to render them oil-wet (the smallest 58 wt% of sand grains were treated). The behavior of this fines-treated sandpack is sig-

nificantly different from that of the sandpack where 50% of all grain sizes were treated to render them oil-wet. At low capillary pressure, the fines-treated curve lies below the uniformly treated one. As the capillary pressure is increased, the fines-treated curve becomes nearly vertical at a much higher water saturation, demonstrating that both the location and fraction of the preferentially water- and oil-wet surfaces are important.

Several researchers have reported behavior similar to that of the fines-treated pack when comparing capillary pressure behavior in native-state, mixed-wet plugs vs. the same plugs when cleaned and rendered water-wet.⁵⁹⁻⁶³ An example is shown in Fig. 9, taken from Richardson *et al.*,⁶⁰ which compares the capillary pressure measured on a native-state plug from the east Texas Woodbine reservoir with the capillary pressure measured on the same plug after it was cleaned and rendered water-wet. Native-state Woodbine core was later shown by Salathiel⁵⁵ to have mixed wettability, with large oil-wet pores and small water-wet ones. Similar behavior for cleaned vs. native-state core can be found in Rühl *et al.*,^{61,62} Schmid,⁶³ and Luffel and Randall.⁵⁹

After the native-state curve shown in Fig. 9 was measured, the plug was cleaned and dried. It was then saturated with brine, and a capillary pressure curve starting from a 100% brine saturation was measured. The behavior of this plug in the native vs. cleaned states is very different from the behavior of neutrally or fractionally wetted plugs shown in Figs. 6 and 7. At low capillary pressures, the native-state capillary pressure curve in Fig. 9 is lower than the cleaned water-wet one. It then crosses over with a higher IWS, which is in better agreement with the IWS measured by oilflooding a native-state core.^{55,60} In contrast, the IWS for a neutral or fractionally wet core is the same as or slightly lower than the IWS when the core is water-wet.

Schmid⁶³ pointed out that mixed wettability is responsible for the capillary pressure behavior of these cores. At the beginning of the capillary pressure measurement in the mixed-wettability (native-state) plug, oil enters the large oil-wet pores. A lower capillary pressure is required to displace the water from the large pores when they are oil-wet vs. water-wet, so the capillary pressure curve is initially below that of the cleaned water-wet core. During this time, some of the water in the small pores is bypassed and trapped. Eventually, most of the water in the large oil-wet pores is displaced, and oil begins to enter the remaining smaller pores, which are water-wet and filled with water. At this point, the capillary pressure for the mixed-wettability core crosses over the cleaned curve and begins to rise rapidly. This occurs for two reasons. First, a higher capillary pressure is required to force oil into the smaller water-wet pores. Second, the IWS will be relatively high because some of the water in the small water-wet pores will have a tendency to be bypassed and trapped as oil flows in the larger pores.

Effects of Surface Roughness on Apparent Contact Angle

The experiments discussed above show that in uniformly wetted cores, the capillary pressure is insensitive to the contact angle for a surprisingly large range of contact angles. Imbibition results are the same as the zero-contact-

angle case when the contact angle is less than about 22° [0.38 rad],^{28,29} and drainage results are the same when the contact angle is less than about 50° [0.87 rad].^{25,26,28,29,41,48} At larger contact angles, there is an effect of contact angle on wettability, but it is not the cosine relationship predicted by the capillary tube bundle model.

There appear to be several reasons why capillary pressure, particularly drainage capillary pressure, is relatively insensitive to contact angle. The first reason is that use of a $\cos \theta$ factor assumes that the porous medium can be modeled as a bundle of circular capillary tubes. Departure of the pore geometry from this assumption, however, will alter the effects of contact angle on capillary pressure.^{64,65} Branches, side pore mouths, and void spaces can greatly affect the interface shape and the apparent contact angle.^{48,66} Second, reservoir rocks contain a large number of sharp edges. On a smooth surface, the contact angle is fixed; however, on a sharp edge, this condition is relaxed, and there is a wide range of permissible contact angles.^{19,28,67} The angle that a fluid/fluid interface makes at such a sharp edge depends on fluid saturations and the geometry over the entire pore, rather than just local surface conditions.⁶⁸ Morrow¹⁹ postulates that many of the oil/water/rock contact lines in a core will be located at sharp edges because here the contact angle can change without moving the position of the oil/water/rock contact.

The third reason for insensitivity to contact angle is the rough surfaces of the cores.^{41,48,67} Surface roughness diminishes the apparent contact angle when the contact angle measured on a flat plate is less than 90° [1.57 rad] and increases the apparent contact angle when the true contact angle is greater than 90° [1.57 rad]. For example, Tamai and Aratani⁶⁹ measured the contact angle of mercury on silica glass surfaces. When the glass had a mirror-smooth finish, the contact angle was 129° [2.25 rad]. The apparent macroscopic contact angle increased to 155 to 160° [2.71 to 2.79 rad] when the silica surface was roughened. Good and Mikhail⁴⁸ recently observed apparent contact angles of mercury on the surface of cement paste (which is microscopically very rough) of 170 to 175° [2.97 to 3.05 rad].

The effects of surface roughness on apparent contact angle for preferentially wetting and nonwetting drops is shown in Fig. 10.⁷⁰ θ_T is the contact angle measured on a smooth surface, and θ_a is the apparent contact angle measured from the droplet to a horizontal plane. In Fig. 10a, the drop is the preferentially wetting phase. The drop is stable in the configuration shown, with the contact line on the inner surface of the roughness "peaks." The apparent contact angle, θ_a , is less than the true contact angle, demonstrating that roughness decreases the apparent contact angle when θ_T is less than 90° [1.57 rad]. In Fig. 10b, the drop is the preferentially nonwetting phase ($\theta_T > 90^\circ$ [1.57 rad]). In this case, the stable contact line is on the outside of the peaks, making the apparent contact angle greater than θ_T .

One equation for the effects of surface roughness on apparent contact angle is Wenzel's equation^{6,70,71}:

$$\cos \theta_a = B \cos \theta_T \dots \dots \dots (20)$$

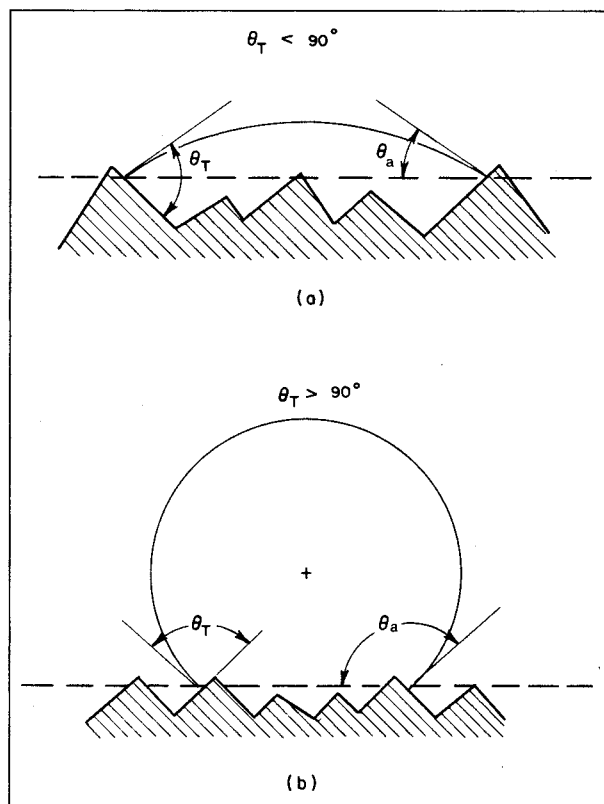


Fig. 10—Effects of surface roughness on apparent contact angle θ_a . θ_T is the contact angle measured on a smooth, flat surface. (a) The droplet is the preferentially wetting fluid, so $\theta_T < 90^\circ$. (b) The droplet is the nonwetting fluid, so $\theta_T > 90^\circ$.⁷⁰

B is a roughness ratio defined by

$$B \equiv \frac{A}{A'}, \dots \dots \dots (21)$$

where A is the true area of the surface, taking into account all of the peaks and valleys, and A' is the projected flat area of a plane with the same dimensions as A .

Note that the apparent contact angle will be 0 or 180° [0 or 3.14 rad] when r is sufficiently large. For example, the apparent contact angle for mercury ($\theta_T = 140^\circ$ [2.44 rad]) will be 180° [3.14 rad] when r is greater than 1.3 . Wenzel's equation gives an idea of the effects of roughness on contact angle. It is only an approximation, however, and does not hold for all rough surfaces.^{8,30,72-74}

Variations in the wettability of the porous surface, such as occur in fractional- and mixed-wet cores, will also affect the apparent contact angle. On a fractionally wetted surface, the contact angle depends on the distribution and amounts of the differently wetted surfaces. Discussion of these fractional wettability effects for smooth surfaces can be found in Refs. 8 and 75. However, I am not aware of any work for rough surfaces or porous media.

Effects of Wettability on Irreducible Saturations

Both irreducible wetting- and nonwetting-phase saturations depend on wettability, pore structure, and saturation history. We will first discuss experiments on

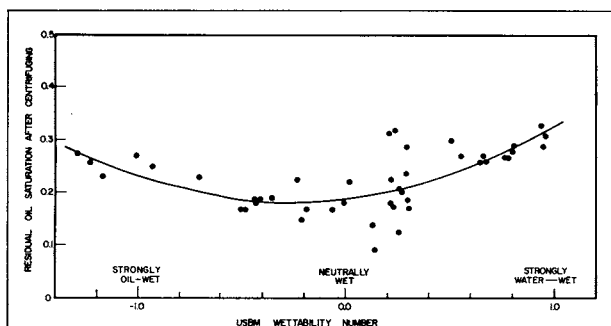


Fig. 11—Average ROS after centrifuging vs. USBM wettability index. Squirrel oil and organochlorosilane-treated Torpedo sandstone cores, 77°F. Curve is a least-squares fit.⁷⁶

uniformly wetted cores, which show that the minimum irreducible saturation occurs when the system is near neutral wettability. However, this finding does not apply in fractional- or mixed-wet systems or in very homogeneous porous media such as bead packs.

Uniformly Wetted Systems. Reservoir Cores. Fig. 11, taken from Lorenz *et al.*,⁷⁶ shows the variation of the irreducible saturation with wettability in reservoir rock using crude oil. The centrifuge method was used to create the capillary pressures applied to the core. (Note that the residual saturation data presented by Lorenz *et al.*,⁷⁶ McGhee *et al.*,⁷⁷ and Charlesworth⁷⁸ refer to the average saturation of the core, not the face saturation determined by the method of Hassler and Brunner⁷⁹ and Slobod *et al.*⁸⁰ In these data, an assumption has been made that the capillary pressure is high enough for the average and face saturations to be essentially equal.) In these tests, the wettability was varied with different concentrations of Drifilm and assessed by the USBM wettability index, W .⁸¹⁻⁸³ A W of 0 is the dividing line between wetting preference. For $W < 0$, oil is the wetting fluid, whereas for $W > 0$, water is the wetting fluid. The further W is from zero, the greater the wetting preference. As can be seen in Fig. 11, the ROS decreases from roughly 30% when the core is strongly water- or oil-wet to about 20% when the system is neutrally wet. The curve reaches a minimum at a slightly oil-wet condition, when W is slightly less than zero.

Similar results for the irreducible wetting-phase saturation were obtained by Morrow and Mungan,²⁸ as shown in Fig. 12. As discussed earlier, they used pure fluids and sintered teflon cores. Contact angles near 0° correspond to W near 1, while contact angles near 90° [1.57 rad] correspond to W near 0. Again, the residual wetting-phase saturation decreased from around 30% to approximately 20% as the system approached neutral wettability. These data may show a minimum near $\theta = 90^\circ$ [1.57 rad] at neutral wettability, although there are not enough data to be certain.

McGhee *et al.*⁷⁷ measured the irreducible nonwetting phase and obtained results similar to Lorenz *et al.* Clean Berea cores were saturated with brine, driven to IWS with the crude oil to be tested, aged at 140°F [60°C] for 1,000

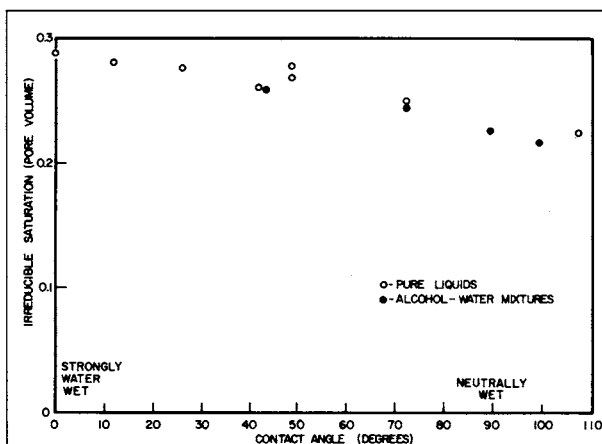


Fig. 12—Irrducible wetting-phase saturation vs. contact angle, teflon cores.²⁸

hours to reach wetting equilibrium, and then assayed for the USBM wettability index and irreducible oil saturation. They found that the irreducible nonwetting (oil) saturation decreased from 0.35 to 0.1 as the USBM wettability index was reduced from 1 (water-wet) to 0 (neutrally wet).

Charlesworth⁷⁸ also examined the effects of wettability on the ROS. His results will not be discussed here, however, because of problems with his experimental procedure. During his measurements, Charlesworth continually accelerated his centrifuge up to its maximum speed, then decelerated it to make measurements. The possibility of fluid redistribution during the deceleration makes any interpretation of his data very questionable.⁷⁹

For the experiments discussed above, capillary forces dominate the processes that trap residual oil. Both buoyancy and viscous forces are so small in comparison that they may be neglected. In waterflooding experiments, capillary forces also dominate trapping. Because the forces that determine the residual fluid distribution are the same, one would also expect that capillary pressure residual saturation would be similar to the residual saturation achieved after waterflooding a core with many PV's of water. For example, Kennedy *et al.*⁸⁴ waterflooded chemically consolidated sandpacks with wettabilities that ranged from water-wet to oil-wet. They found that the minimum ROS occurred when the system was slightly oil-wet. Further discussion of the effects of wettability on waterflood ROS can be found in Ref. 5.

Beads and Sandpacks. There is a strong interaction between wettability and pore geometry in determining when a fluid becomes discontinuous and the irreducible saturation is reached. The data of Lorenz *et al.*,⁷⁶ McGhee *et al.*,⁷⁷ Morrow and Mungan,²⁸ and Mungan²⁹ show the importance of wettability when the geometry is sufficiently complicated. In such cases, small-scale heterogeneities aid in trapping the fluid.⁸⁵ If the geometry is sufficiently simple, however, wettability effects may become unimportant. Such simple geometries include beads and sandpacks, where the residual saturation is typically very low (less than 10%) and only slightly influenced by wettability.^{37,86,87}

Morrow⁸⁶ examined the irreducible wetting-phase saturation of pure fluids in random packings of equal-size teflon spheres. In this case, the irreducible saturation took

the form of pendular rings,^{7,18} which are disconnected rings of fluid wrapped around the contact point between two adjacent spheres. For this simple core geometry, Morrow found little variation in the irreducible saturation as the wettability was varied. For variations in θ ranging from 0 to 108° [0 to 1.88 rad], S_w was always in the range of $7.5 \pm 1.5\%$. Von Engelhardt⁸⁷ and Harris *et al.*³⁷ have also reported very little effect of wettability on irreducible saturation in their packed beds.

One exception to these findings is the experiments of Bethel and Calhoun,³³ who used n-octane to displace water from glass bead packs. The wettability was varied by treating the beads with different concentrations of Drifilm to render them more oil-wet. The irreducible saturation decreased from about 35 to 15% PV as the beads became less water-wet.

Fractional and Mixed Wettability. Some disagreement exists on the effects of wettability on irreducible wetting-phase saturation in fractionally wetted packs when the strongly water-wet and strongly oil-wet grains are distributed randomly.^{56-58,86} Morrow⁸⁶ found little effect of fractional wettability on the IWS in packs composed of teflon (oil-wet) and glass (water-wet) beads. The irreducible saturation was reached by letting air replace water as it drained from the pack. The IWS's for 100% teflon beads, 100% glass beads, and a 50/50 mixture were essentially equal for this very simple, homogeneous geometry.

As discussed earlier, Fatt and Klikoff⁵⁶ measured oil/brine capillary pressures in fractionally wetted sandpacks and found only a small effect of wettability on the IWS when all of the particle sizes had equivalent amounts of water-wet and oil-wet grains (see Figs. 7 and 8).

In Fig. 7, the IWS for the 100% water-wet sandpack may be higher than the others, although it is difficult to be sure because the curves stop at relatively low capillary pressures. In Fig. 8, with a wider distribution of sand grain sizes, the IWS for the 100% water-wet and the 50/50 packs are essentially equal. On the other hand, Talash and Crawford^{57,58} found that the IWS decreased from about 17 to 6% PV as the percentage of oil-wet sand grains increased from 0 to 75%.

The above experiments were for fractionally wetted systems in which the water-wet and oil-wet grains were distributed randomly. Additional wettability effects will occur in fractional and mixed systems when the water- and oil-wet surfaces are organized in some fashion. Fig. 8 compares the behavior of a sandpack with a random distribution of oil- and water-wet surfaces vs. the fines-treated pack, where the smallest grains are oil-wet, while the large ones are water-wet.⁵⁶ The IWS of the fines-treated core is about 40%, while for the random pack it is less than 20%.

Mixed-wettability cores have a much higher IWS than the same cores after they are cleaned and made uniformly water-wet.⁵⁹⁻⁶³ In contrast, recall that in the uniformly wetted systems discussed above, the IWS was lower in neutrally wet cores than it was in strongly water-wet ones. Fig. 9, taken from Richardson *et al.*,⁶⁰ compares the capillary pressure measured on a single core, first in its native mixed-wettability state, then after the core was cleaned and rendered water-wet. The higher IWS in mixed-wet vs. water-wet cores is a result of faster trap-

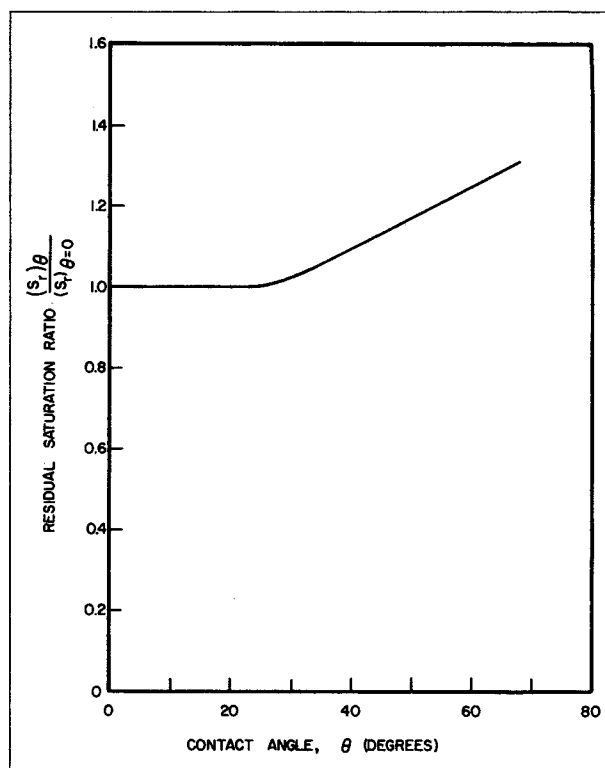


Fig. 13—Zero-capillary-pressure nonwetting saturation vs. contact angle, teflon cores.²⁹

ping and loss of hydraulic continuity. This was discussed previously in the section on experiments in fractional- and mixed-wet systems.

Displacement Capillary Pressure and Imbibition

Uniformly Wetted Systems. Consider a core initially containing a low wetting-phase saturation. If the wetting preference of the rock surface is great enough, capillary forces will cause the wetting fluid to imbibe spontaneously into the core, displacing the nonwetting one. Imbibition is driven by the favorable surface free energy change that occurs when the wetting fluid displaces the nonwetting one.⁸⁸ The rate and amount of imbibition depend on the wettability, viscosity, IFT, pore structure, saturation history, and initial saturation of the core.^{7,89}

When the core is strongly wetted, a large volume of wetting fluid imbibes rapidly because of the large decrease in the surface free energy. After the imbibition is complete, a strongly wetted core is essentially at the irreducible nonwetting-phase saturation.^{7,12} In contrast to the spontaneous imbibition of the wetting fluid, a relatively high capillary pressure is necessary to force the nonwetting fluid into the core because this change increases the surface free energy of the system. In particular, a positive capillary pressure, known as the displacement or threshold capillary pressure, must be applied before the nonwetting fluid will begin to enter a core initially 100% saturated with the wetting fluid.

As the core becomes less strongly wetted, the energy available for spontaneous imbibition decreases. A smaller amount of wetting fluid will imbibe at a slower rate into

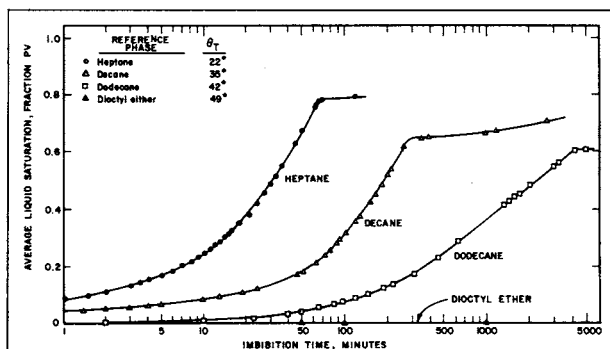


Fig. 14—Spontaneous imbibition of liquids into a teflon core initially air saturated.⁵⁰

the core. At the same time, the displacement pressure to force the nonwetting fluid into the core also decreases.

As the system approaches neutral wettability, neither fluid will imbibe spontaneously. On the basis of wettability considerations alone, one would predict that spontaneous imbibition would occur for any contact angle less than 90° [1.57 rad] because there is still some driving force for the wetting fluid to displace the nonwetting one. It is found experimentally, however, that spontaneous imbibition in a uniformly wetted core will stop at a much lower contact angle^{51,90} because of the effects of pore structure, and a positive displacement pressure will be required to force both the preferentially wetting and nonwetting fluids into the core. Positive displacement pressures for both fluids, particularly when the core is initially 100% saturated with the other fluid, have frequently been reported in the literature.^{14,15,17,51,90-92} When a positive displacement pressure is required for both fluids, the fluid with the lower displacement pressure is the preferentially wetting fluid because less energy is required to force it into the core.^{16,90}

Morrow and Mungan²⁸ and Morrow²⁹ measured the zero-capillary-pressure nonwetting saturation using pure fluids in a teflon core. The capillary pressure, initially at a high positive value, was gradually lowered to zero as the wetting fluid imbibed. The results, normalized to the residual saturation obtained when the contact angle was zero, are shown in Fig. 13. This nonwetting-phase residual saturation increases as the contact angle increases, which is the exact opposite of the behavior for the irreducible nonwetting saturation (see Fig. 11). Note that the nonwetting phase at zero capillary pressure is generally still connected, so this residual saturation is not irreducible.

The experiments above measured the amount of spontaneous imbibition when the capillary pressure was reduced from a large, positive value to zero in a quasistatic manner. A second type of experiment that measures both imbibition volume and rates will be referred to here as free imbibition. In these experiments, a plug with a low wetting-phase saturation is immersed in the wetting fluid, while the amount and rate of spontaneous imbibition is measured. In free imbibition, there is no applied capillary pressure.

McCaffery *et al.*⁵⁰⁻⁵² measured the rate and volume of countercurrent free imbibition in teflon cores with air

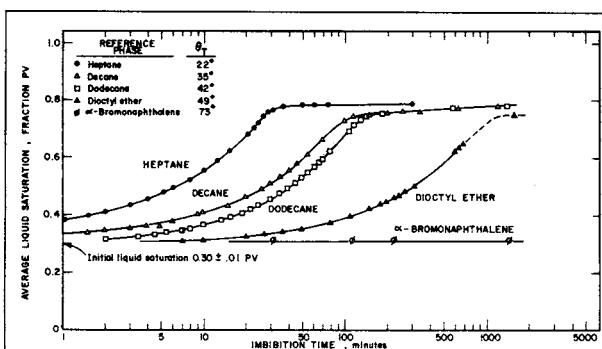


Fig. 15—Spontaneous imbibition of liquids into a teflon core. The core initially contained air and a liquid saturation of 0.30 ± 0.01 PV.⁵⁰

and different pure fluids. The results are shown in Figs. 14 and 15.⁵⁰ Fig. 14 shows the results for imbibition of several fluids into an initially dry (air-saturated) core. The imbibition rate becomes slower and the amount imbibed smaller as the contact angle increases and the favorable change in surface free energy decreases. Note that dioctyl-ether ($\theta = 49^\circ$ [0.85 rad]) was unable to imbibe.

Fig. 15 shows the results for free imbibition of the fluids into a core with an initial wetting fluid saturation of about 30% PV. Imbibition rates were much faster when compared with the dry core. Again, the imbibition rate slowed as the liquid/air/teflon system became more neutrally wet. In contrast to Fig. 14, however, the final saturation was similar for all fluids that could imbibe. When an initial saturation of 30% PV was present, dioctyl-ether was able to imbibe slowly into the core. Apparently, the presence of an initial connected saturation was necessary for dioctyl-ether to imbibe. On the other hand, α -bromonaphthalene ($\theta_T = 73^\circ$ [1.27 rad]) was never able to imbibe, whatever the initial saturation of the core.

A number of wettability measurement systems, such as the Amott⁹³ method, are based on free imbibition rates or volumes.^{2,94} The results of McCaffery *et al.* show that there is a large range of contact angles for which neither fluid will imbibe and that the cutoff depends on the initial wetting-phase saturation. Dioctyl-ether would not imbibe into a dry core, whereas α -bromonaphthalene would never imbibe. These systems would be classified as neutrally wet by imbibition tests.

The interaction of wettability and pore structure is responsible for the failure of spontaneous imbibition as the contact angle is increased. The apparent contact angle in a porous medium often differs substantially from the contact angle measured on a smooth surface or in a circular capillary tube. Calculations for pore geometries consisting of cones,⁶⁴ toroidal (doughnut-shaped) pores,^{11,95} grids,^{66,96} and packed spheres^{23,97,98} all show a strong interaction between contact angle and geometry in determining the capillary-pressure/saturation relationship. For example, Melrose²³ calculated that the wetting phase would not imbibe into a porous medium composed of packed spheres when the contact angle was greater than roughly 40° [0.7 rad].

As a second example, the apparent contact angle is generally larger than the true contact angle for a drop on a porous surface (the drop acts less wetting) because of

the interaction of pore structure and wettability.^{6,66,96} The surface of a porous medium is composite because it consists of small patches of solid surfaces and holes. One expression for the apparent contact angle on a porous surface was given by Cassie and Baxter⁶⁶:

$$\cos \theta_a = f_1 \cos \theta_T - f_2, \dots \dots \dots (22)$$

where f_1 is the fraction of solid area and f_2 is the fraction of open area. It can be seen that the apparent contact angle increases as the fraction of open area increases.

Fractional and Mixed Wettability. Unfortunately, there have been very few imbibition measurements in systems with fractional or mixed wettability. Experiments in fractionally wetted sandpacks indicate that water imbibition into the pack will stop when more than 50% of the surfaces are oil-wet (or oil imbibition will stop when 50% or more of the surfaces are water-wet).^{63,99} Gimatudinov⁹⁹ measured the initial free imbibition rate into fractionally wetted sandpacks initially 100% saturated with oil. He found that the imbibition rate decreased rapidly as the fraction of oil-wet grains increased and stopped when 50% of the grains were oil-wet. The rate was affected by as little as 5% oil-wet grains.

Amott⁹³ used his wettability measurement method to measure the free imbibition volume into fractionally wetted sandpacks. The sandpacks were initially at irreducible saturation, and the volume of fluid that imbibed after 20 hours was measured. The oil (and water) imbibition volume was reported as the displacement-by-oil (displacement-by-water) ratio, which is normalized with the total volume of oil (water) that is forced into the core during imbibition and centrifugal displacement. Amott found that water but not oil would imbibe into a fractionally wetted sandpack when more than 50% of the grains were water-wet. Similarly, only oil would imbibe into packs when more than 50% of the grains were oil-wet. Amott found little or no effect of fractional wettability on the normalized imbibition volume when less than 25% of either sand was added to the other sand. The normalized imbibition volumes were essentially the same as when the pack consisted of a single sand, either water- or oil-wet. As the proportion of sand with opposite wettability was increased from 25 to 50%, the imbibition volume decreased to zero almost linearly.

Finally, note that in fractional- and mixed-wettability cores, it may be possible for both fluids to imbibe spontaneously (starting from an initially low saturation of that fluid).^{100,101} Burkhardt *et al.*¹⁰² found that preserved east Texas Woodbine plugs would imbibe both water and oil. Preserved plugs were driven to ROS with brine and allowed to imbibe kerosene. The plugs were then driven to IWS with kerosene and allowed to imbibe brine. Average amounts of oil and brine imbibition were 10.2 and 7.1% PV, respectively. The east Texas Woodbine reservoir was later shown by Salathiel⁵⁵ to have mixed wettability.

Mohanty and Salter¹⁰⁰ generated mixed-wettability cores, where the large pores have continuous water-wet surfaces while the small pores are oil-wet. Note that the wettability in these cores is reversed from Salathiel's⁵⁵ mixed-wettability cores. The wettability was measured with the Amott method. The displacement-by-water ra-

tio was roughly 0.3, and the displacement-by-oil ratio was roughly 0.8, indicating that substantial volumes of both oil and water could imbibe into the core.

Possible Errors Caused by Using Cleaned Cores

Several errors are introduced into the interpretation of capillary pressure measurements when a core is cleaned and made water-wet but the reservoir is actually intermediate or oil-wet. The first is that the shape of the capillary pressure curve will change, causing an overestimation of the height of the transition zone. This can be seen in Fig. 6a, where the relative shapes of the curves change as the contact angle increases.

The second possible error is misestimation of the interstitial water saturation. Fig. 11 shows that the irreducible saturation for uniformly wetted cores has a minimum near neutral wettability. The interstitial water at reservoir conditions can be higher or lower than the IWS of the clean core, depending on how water-wet the cleaned core is compared to the native conditions. This is particularly important when the native core has fractional or mixed wettability.

Finally, when waterflooding fractured reservoirs, the recovery in the matrix blocks is controlled by capillary forces and gravity. In a water-wet rock, capillary forces will aid drainage of the oil, while in an oil-wet rock they can retard it.¹⁰³ Ignoring wettability conditions can result in an overestimation of the oil that can be recovered by imbibition and make overly optimistic assumptions about the drainage rate.

Conclusions

1. The capillary-pressure/saturation relationship depends on the interaction of wettability, pore structure, and saturation history. No simple relationship exists that relates the capillary pressures determined at two different wettabilities. In particular, a porous medium can generally not be modeled as a set of capillary tubes. Because there is no simple relationship, an apparent contact angle calculated from either the displacement capillary pressure or the complete capillary pressure curve is only a rough estimate of the actual contact angle.

2. In a uniformly wetted porous medium, the drainage capillary pressure is insensitive to the wettability when the contact angle is less than 50° [0.87 rad]. This has been demonstrated in measurements with uniformly wetted teflon cores and by use of mercury capillary pressure measurements with reservoir cores. This insensitivity is a result of pore geometry effects and the extremely rough surfaces of the porous medium, which makes the effective contact angle zero. Similarly, the spontaneous-imbibition capillary pressure curve (positive capillary pressure) measured in a uniformly wetted core is insensitive when the contact angle is less than about 20° [0.35 rad].

3. The most accurate capillary pressure measurements are made on native- or restored-state cores with crude oil and water because these conditions best match those in the reservoir. While measurements with cleaned cores or with other fluids such as air/water or mercury/vacuum can be made, there is no simple relationship (cosine or otherwise) to convert to the native-state oil/water capil-

lary pressure curves. Generally, measurements with fluids like air/water or mercury/vacuum where one of the fluids is strongly wetting will give accurate results only in strongly water-wet reservoirs. The contact angle should be neglected when converting to the oil/brine capillary pressure, as shown by the experiments in uniformly wetted porous media discussed previously.

4. The minimum ROS occurs when a uniformly wetted system is slightly oil-wet to neutrally wet. This residual saturation correlates well with the residual saturation that occurs in waterflooding after many PV's of water have been flowed through the system. If the reservoir has a fractional or mixed wettability, then residual saturations depend on both the amount and distribution of the water-wet and oil-wet surfaces.

5. When a system is strongly wetted, the preferential wetting fluid will spontaneously imbibe into the core, displacing the nonwetting fluid. The amount and rate of spontaneous imbibition depends on the wettability, viscosity, IFT, pore structure, and initial saturation of the core. Wettability (surface energy) considerations alone would indicate that at least some imbibition would occur when the contact angle is less than 90° [1.57 rad]. There is no free imbibition, however, in an initially dry, uniformly wetted teflon core when the contact angle is as low as 49° [0.86 rad]. This implies that in a uniformly wetted reservoir core, there is a large range of contact angles where neither oil nor water will imbibe spontaneously.

6. In a fractional- or mixed-wet core, it is possible for either fluid to imbibe freely when the core is initially at the irreducible saturation for that fluid.

7. If the reservoir is intermediate- or oil-wet and a clean water-wet core is used, the shape of the capillary pressure curve will not be representative of the reservoir. This causes an overestimation of the height of the transition zone and an inaccurate estimation of the interstitial water.

8. Measurements made with a clean water-wet core will overestimate the amount and rate of oil recovered by imbibition when waterflooding a non-water-wet reservoir, especially a fractured one.

Nomenclature

- A = true area of a rough surface, taking into account all of the peaks and valleys
- A' = projected flat area of a plane with the same dimensions as A
- B = roughness ratio, A/A'
- f_1 = fraction of solid area
- f_2 = fraction of open area
- F = scaling factor, Eqs. 17 through 19
- h = height of the interface in the capillary tube
- J = Leverett J function
- k = absolute permeability
- p_{NW} = pressure in the nonwetting fluid
- p_o = pressure in the oil
- p_w = pressure in the water
- p_{WET} = pressure in the wetting fluid
- P_c = capillary pressure
- P_{dr} = drainage capillary pressure
- P_{imb} = imbibition capillary pressure
- r = radius

- r_s = radius of a spherical interface, Fig. 1
- r_t = radius of a capillary tube
- r_1, r_2 = radii of curvature of the interface, measured perpendicular to each other
- S_o = oil saturation
- S_r = reference phase saturation
- S_w = water saturation
- V_b = bulk volume
- W = USBM wettability index
- ΔW_{ext} = external work
- θ = contact angle
- θ_a = apparent contact angle
- θ_{adv} = advancing contact angle, measured on a rough surface
- θ_{rec} = receding contact angle, measured on a rough surface
- θ_T = true contact angle, measured on a smooth, flat surface
- σ = IFT
- ϕ = porosity

Subscripts

- aw = air/water
- Hg = mercury

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SI Metric Conversion Factors

degrees	× 1.745 329	E-02 = rad
ft	× 3.048*	E-01 = m
°F	(°F-32)/1.8	= °C
in.	× 2.54*	E+00 = cm
psi	× 6.894 757	E+00 = kPa

*Conversion factor is exact.

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Wettability Literature Survey— Part 5: The Effects of Wettability on Relative Permeability

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Summary. The wettability of a core will strongly affect its waterflood behavior and relative permeability. Wettability affects relative permeability because it is a major factor in the control of the location, flow, and distribution of fluids in a porous medium. In uniformly or fractionally wetted porous media, the water relative permeability increases and the oil relative permeability decreases as the system becomes more oil-wet. In a mixed-wettability system, the continuous oil-wet paths in the larger pores alter the relative permeability curves and allow the system to be waterflooded to a very low residual oil saturation (ROS) after the injection of many PV's of water. The most accurate relative permeability measurements are made on native-state core, where the reservoir wettability is preserved. Serious errors can result when measurements are made on cores with altered wettability, such as cleaned core or core contaminated with drilling-mud surfactants.

Introduction

This paper is the fifth in a series of literature surveys covering the effects of wettability on core analysis.¹⁻⁵ Wettability has been shown to affect waterflood behavior, relative permeability, capillary pressure, irreducible water saturation (IWS), ROS, dispersion, simulated tertiary recovery, and electrical properties. Earlier, but less complete, reviews covering the effects of wettability on waterflood and relative permeability can be found in Refs. 6 through 16.

Relative permeability is "a direct measure of the ability of the porous system to conduct one fluid when one or more fluids are present. These flow properties are the composite effect of pore geometry, wettability, fluid distribution, and saturation history."⁶ Wettability affects relative permeability because it is a major factor in the control of the location, flow, and spatial distribution of fluids in the core. Craig⁶ and Raza *et al.*¹⁰ have given good summaries of the effects of wettability on the distribution of oil and water in a core. Most experimental studies that examined fluid distribution as a function of wettability used bead packs or other micromodels,¹⁷⁻²⁴ although some more recent studies have used reservoir rock and fluids such as epoxy or Wood's metal that can be solidified in situ (e.g., see Yadav *et al.*²⁵).

Consider a strongly water-wet rock initially at IWS. Water, the wetting phase, will occupy the small pores and form a thin film over all the rock surfaces.^{19,20,22,26,27} Oil, the nonwetting phase, will occupy the centers of the larger pores. This fluid distribution occurs because it is the most energetically favorable. Any oil placed in the small pores would be displaced into the center of the large pores by spontaneous water imbibition, because this would lower the energy of the system.

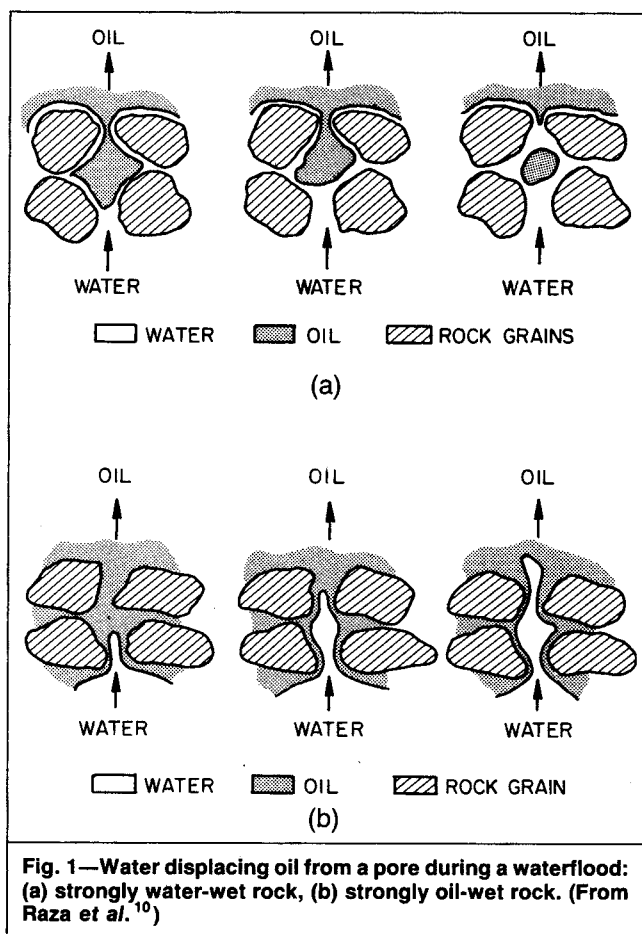
During a waterflood of a water-wet system, water moves through the porous medium in a fairly uniform front.⁶ The injected water will tend to imbibe into any small- or medium-sized pores, moving oil into the large pores where it is easily displaced. Only oil is moving ahead of the front. In the frontal zone, each fluid moves through its own network of pores, but with some wetting fluid located in each pore.⁶ In this zone, where both oil and water are flowing, a portion of the oil exists in continuous channels with some dead-end branches, while the remainder of the oil is trapped in discontinuous globules. Fig. 1a, taken from Raza *et al.*,¹⁰ shows water displacing oil from a water-wet pore. The rock surface is preferentially wetted by the water, so water will advance along the walls of the pore, displacing oil in front of it. At some point, the

neck connecting the oil in the pore with the remaining oil will become unstable and snap off, leaving a spherical oil globule trapped in the center of the pore. After the water front passes, almost all the remaining oil is immobile. Because of such immobility in this water-wet case, there is little or no production of oil after water breakthrough.^{6,18-20,22,23,26} The disconnected, residual oil exists in two basic forms: (1) small, spherical globules in the center of the larger pores, and (2) larger patches of oil extending over many pores that are completely surrounded by water.

In a strongly oil-wet rock, the rock is preferentially in contact with the oil, and the location of the two fluids is reversed from the water-wet case. Oil generally will be found in the small pores and as a thin film on the rock surfaces, while water will be located in the centers of the larger pores. The interstitial water saturation appears to be located as discrete droplets in the centers of the pore spaces in some strongly oil-wet reservoirs.¹⁰ A waterflood in a strongly oil-wet rock is much less efficient than one in a water-wet rock. When the waterflood is started, the water will form continuous channels or fingers through the centers of the larger pores, pushing oil in front of it (see Fig. 1b¹⁰). Oil is left in the smaller crevices and pores. As water injection continues, water invades the smaller pores to form additional continuous channels, and the WOR of the produced fluids gradually increases. When sufficient water-filled flow channels form to permit nearly unrestricted water flow, oil flow practically ceases.⁶ The remaining oil is found (1) filling the smaller pores, (2) as a continuous film over the pore surfaces, and (3) as larger pockets of oil trapped and surrounded by water.^{19,20,26} Because much of this oil is still continuous through the thin oil films and can be produced at a very slow rate,^{19,22,23,26} the ROS is not well-defined.

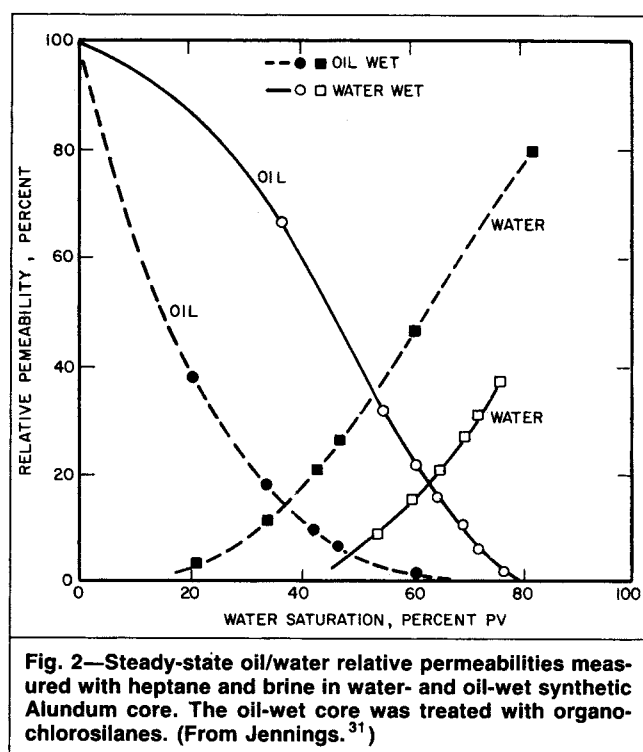
In this paper, the terms "wetting" and "nonwetting" will be used in addition to water-wet and oil-wet. This will more easily enable us to draw conclusions about a system with the opposite wettability. For example, a waterflood in a system of one wettability will behave in the same manner as an oilflood in the same system with the wettabilities reversed. Relative permeability curves will also show that the fluids can exchange positions and flow behavior.^{28,29} Because relative permeability is a function of saturation history, hysteresis in the relative permeability curves is often observed when comparing relative permeabilities measured with increasing vs. decreasing wetting-phase saturations. "Imbibition" is often used to refer to flow that results in increasing wetting-phase saturations, while "drainage" refers to flow with decreasing wetting-phase saturations.⁶ For example, waterflooding a water-wet rock is an imbibition process, while waterflooding an oil-wet rock is a drainage process.

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Relative Permeability Curves in Strongly Wetted Systems

Before discussing how changes in wettability affect relative permeability, we will examine relative permeability curves measured on strongly water-wet and strongly oil-wet systems. The wetting fluid in a uniformly wetted system generally will be located in the smaller pores and as a thin film in the larger pores, while the non-wetting fluid is located in the centers of the larger pores. In general, at a given saturation, the relative permeability of a fluid is higher when it is the nonwetting fluid. For example, the water relative permeability is higher in an oil-wet system than it would be if the system were water-wet. This occurs because the wetting fluid tends to travel through the smaller, less permeable pores, while the non-wetting fluid travels more easily in the larger pores. In addition, at a low nonwetting-phase saturation, the nonwetting phase will become trapped as discontinuous globules in the larger pores. These globules block pore throats, lowering the wetting-phase relative permeability. On the other hand, the nonwetting-phase relative permeability is high because the nonwetting phase flows through the centers of the larger pores. At low wetting-phase saturations, the



nonwetting-phase effective permeability will often approach the absolute permeability, demonstrating that the wetting phase does not greatly restrict the flow of the nonwetting phase.^{6,10,28,30}

Jennings³¹ measured steady-state relative permeabilities in water-wet and oil-wet synthetic AlundumTM (sintered aluminum oxide) cores with brine and heptane. The water-wet Alundum core was fired at 1,832°F [1,000°C] to remove any adsorbed materials, while the oil-wet core was prepared by treating it with organochlorosilanes. Wettability was measured with imbibition tests.² Both cores were then saturated with heptane, and steady-state relative permeabilities were measured with increasing brine saturations. The results are shown in Fig. 2, with the relative permeabilities normalized to the absolute oil permeability at 100% oil saturation. At any given saturation, the water permeability is higher and the oil permeability is lower in the oil-wet core when compared with the water-wet one. The water relative permeability at ROS for the oil-wet core is roughly 80%, while it is less than 40% for the water-wet core. The crossover point, where the water and oil relative permeabilities are equal, occurs at a water saturation of about 35% PV for the oil-wet core and about 65% PV for the water-wet one. Note that the relative permeability curves for the oil-wet and water-wet cores are in good agreement if they are plotted vs. wetting-phase saturation (oil for the oil-wet system, water for the water-wet system), indicating the reversal of the positions and flow behavior of the oil and water.²⁹

Craig⁶ presented several rules of thumb, given in Table 1, that indicate the differences in the relative permeability characteristics of strongly water-wet and strongly oil-wet cores.^{10,29,32} These

TABLE 1—CRAIG'S⁶ RULES OF THUMBS FOR DETERMINING WETTABILITY

	Water-Wet	Oil-Wet
Interstitial water saturation	Usually greater than 20 to 25% PV.	Generally less than 15% PV. Frequently less than 10%.
Saturation at which oil and water relative permeabilities are equal.	Greater than 50% water saturation.	Less than 50% water saturation.
Relative permeability to water at the maximum water saturation (i.e., floodout); based on the effective oil permeability at reservoir interstitial water saturation.	Generally less than 30%.	Greater than 50% and approaching 100%.

rules are demonstrated in Fig. 3, taken from Craig,⁶ which shows examples of relative permeability curves in strongly wetted systems. Fig. 2 also shows the effects of wettability on the crossover point and the maximum water relative permeability (nothing can be said about the interstitial water saturation because the measurements started at 100% oil saturation). A further example is shown in Fig. 4, taken from Donaldson and Thomas.¹⁹ Core 1 is strongly water-wet, while Core 5 is strongly oil-wet. Treiber *et al.*³³ generally found good agreement between contact angle and relative permeability measurements in obtaining a qualitative indication of reservoir wettability. Additional measurements on strongly water-wet and strongly oil-wet systems in agreement with Craig's rules can be found in Refs. 28, 29, 34 (see Refs. 35 and 36), and 37 through 45.

The differences in relative permeabilities measured in strongly water-wet and strongly oil-wet systems are caused by the differences in the fluid distributions. Consider a strongly water-wet core. At the IWS, the water is located in the small pores, where it has very little effect on the flow of oil. Because the water does not significantly block the oil flow, the oil effective permeability is relatively high, often approaching the absolute permeability.^{10,28} In contrast, the effective water permeability at ROS is very low, because some of the residual oil is trapped as globules in the centers of the larger pores, where it is very effective in lowering the water permeability. Therefore, the water permeability at ROS is much less than the oil permeability at IWS, with a ratio of less than 0.3 for a strongly water-wet core. In a strongly oil-wet core, the positions of the two fluids are reversed. The oil permeability at IWS is relatively low because the residual water blocks the oil flow. The water permeability at ROS is high because the residual oil is located in the small pores and as a film on the surface, where it has little effect on the water flow. Consequently, the ratio of the two permeabilities can approach 1 or be even greater. The exact value is variable because waterflooding an oil-wet core is very inefficient, and the ROS and water relative permeability at ROS depend on how many PV's of water are injected.

Craig's second rule of thumb is that the water saturation at which the water and oil relative permeabilities are equal is greater than 50% in a strongly water-wet core and less than 50% in a strongly oil-wet one. The effective (and relative) permeability of a fluid is a function of the mobility of that phase at a given saturation. In turn, the mobility is a function of the wetting properties and of the average cross-sectional area of the fluid channels—i.e., of saturation.²⁷ The wetting fluid has a relatively low mobility compared with the nonwetting fluid because the wetting fluid is located next to the pore walls, while the nonwetting fluid is located in the centers of the pores. Consequently, the cross-sectional area (saturation) of the wetting fluid must be higher at the relative-permeability crossover point to compensate for its lower mobility.²⁷

Craig's final rule of thumb was that the interstitial water saturation was generally less than 15% PV in an oil-wet system and greater than 20 to 25% PV in a water-wet one. For a water-wet rock, the interstitial water saturation fills the small pores and forms a thin film over the rock surfaces; hence, the water saturation is relatively high. On the other hand, the interstitial water saturation in some uniformly, strongly oil-wet rocks is found as discrete droplets in the centers of the larger pores.¹⁰ Because there is no requirement that the water cover the pore surfaces, the interstitial water saturation is usually much lower. Raza *et al.*,¹⁰ however, state that they have found exceptions to this general rule. In addition, the interstitial water saturation is also a function of permeability and pore structure, particularly for water-wet rocks.^{2,10}

Craig's rules of thumb generally give an indication of the rock wettability, but there are exceptions.¹⁰ One reason is that the relative permeability is also dependent on initial saturation and pore geometry. Caudle *et al.*⁴⁶ found that relative permeability curves measured on a water-wet sandstone were dependent on the initial water saturation. Decreasing the initial water saturation changed the location and shape of the curves. Craig⁶ states that the initial water saturation strongly influences relative permeability curves in strongly water-wet rocks, but has little effect on curves measured on oil-wet rocks as long as the initial water saturation is less than approximately 20%.

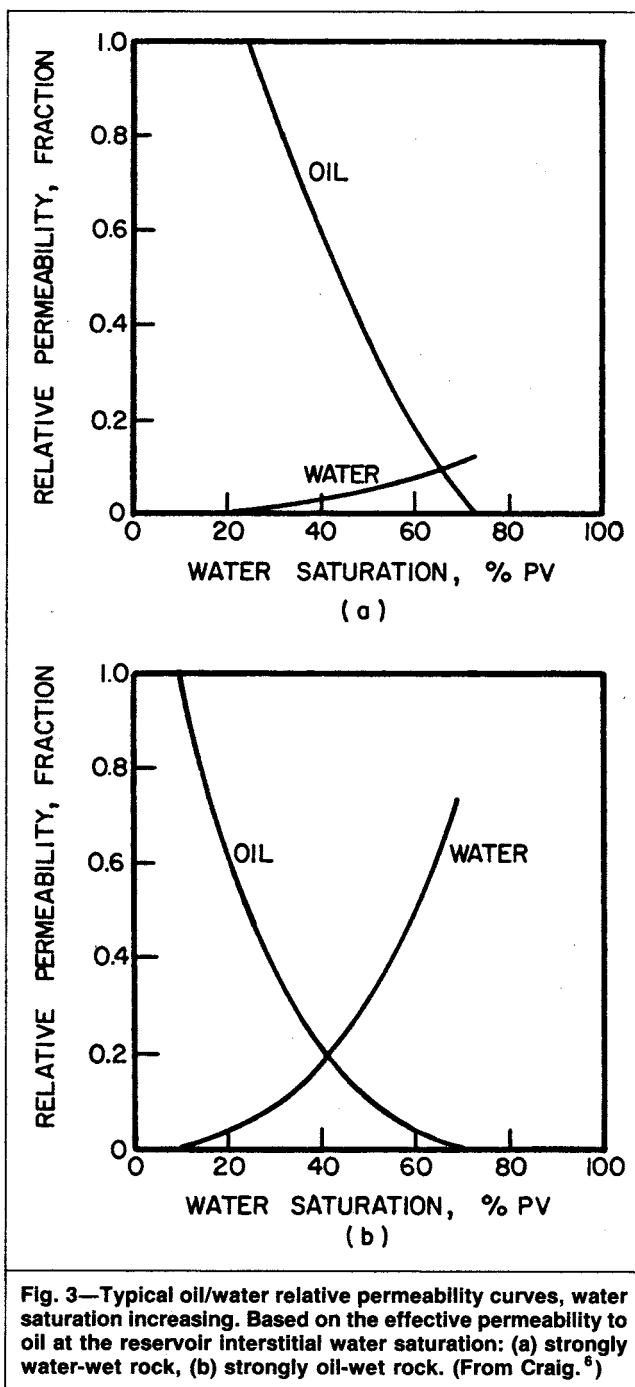


Fig. 3—Typical oil/water relative permeability curves, water saturation increasing. Based on the effective permeability to oil at the reservoir interstitial water saturation: (a) strongly water-wet rock, (b) strongly oil-wet rock. (From Craig.⁶)

Pore geometry can also have a strong effect on the measured relative permeability curves, including such factors as the crossover point and the IWS. Morgan and Gordon⁴⁷ measured relative permeabilities in cleaned, water-wet cores and found significant differences in rocks with large, well-interconnected pores when compared with rocks containing more numerous, smaller, less-well-interconnected pores. In these water-wet cores, the smaller pores are filled with water, which increases the IWS but contributes very little to water flow. When comparing two samples with the same absolute permeability, the rock containing more numerous but smaller pores had a larger IWS and the crossover point for the relative permeabilities occurred at a higher water saturation. Because factors other than wettability can have a similar influence on relative permeability curves, it is preferable to make independent measurements of wettability rather than to rely solely on Craig's rules of thumb to evaluate wettability.

Drainage and Imbibition Relative Permeabilities. In many strongly wetted systems, the wetting-phase relative permeability is primarily a function of its own saturation; i.e., the hysteresis between the

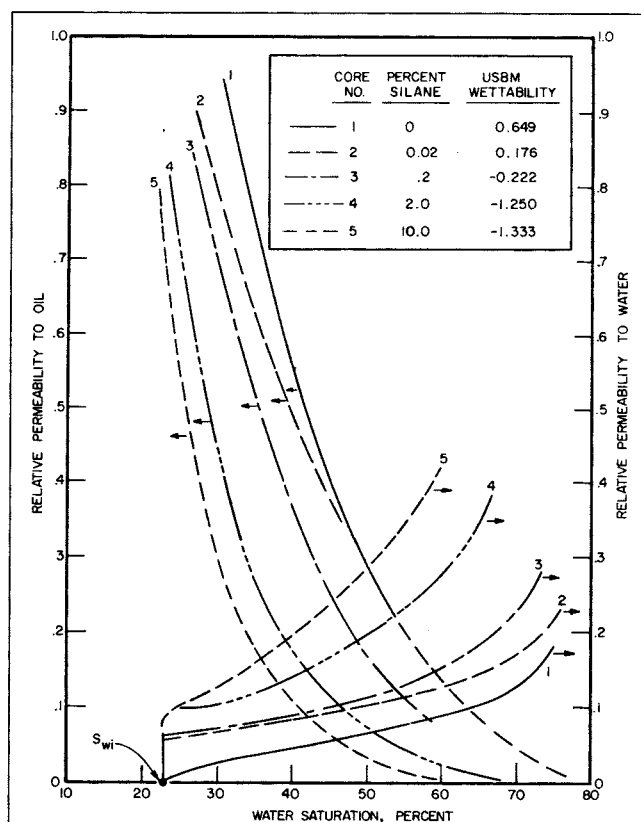


Fig. 4—Effects of wettability on relative permeability using brine, Squirrel crude oil, and organochlorosilane-treated outcrop Torpedo sandstone. Relative permeabilities are based on the absolute water permeability of the 100% brine-saturated core. (From Donaldson and Thomas.¹⁹)

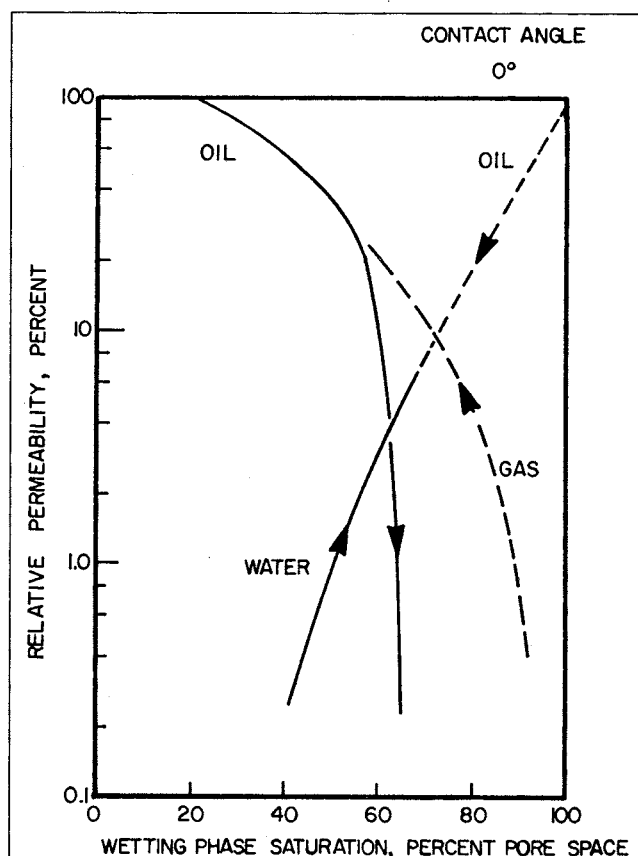


Fig. 5—Comparison of gas/oil drainage and water/oil imbibition relative permeability relationships—strongly water-wet Torpedo sandstone. (From Owens and Archer.⁵¹)

wetting-phase drainage and imbibition relative permeabilities is much smaller than the nonwetting-phase hysteresis.^{33,48-53} In addition, wetting-phase relative permeabilities are very similar for both two- and three-phase relative permeability measurements in strongly wetted systems at a given wetting-phase saturation. In Fig. 5, Owens and Archer⁵¹ compare unsteady-state gas/oil drainage with steady-state water/oil imbibition relative permeabilities in a strongly water-wet Torpedo sandstone core. The oil/water measurements used a refined mineral oil and brine with a small amount of Orvus KTM liquid (a water-wetting detergent) added. The water/oil contact angle measured on a quartz crystal was 0°, indicating that the oil/brine/Torpedo-sandstone system was strongly water-wet. (Note that “water-wet” refers to the wetting preference of the rock for water over oil. Gas is almost always a nonwetting phase for both gas/brine and gas/oil relative permeability measurements.) The gas/oil drainage relative permeabilities, where oil is the strongly wetting fluid, are shown as dotted lines in Fig. 5. The water/oil relative permeabilities, where water is the strongly wetting fluid, are shown as solid lines. Note that the water relative permeability, where the wetting-fluid saturation is increasing, is a continuation of the oil relative permeability, where the wetting-fluid saturation is decreasing.

Treiber *et al.*³³ also compared steady-state water/oil and unsteady-state gas/oil relative permeabilities and found good qualitative agreement with wettabilities measured by contact angles. In a water-wet system, they found good agreement between the wetting-phase relative permeabilities: water in the water/oil tests and oil in the gas/oil tests. The water saturation increased during the water/oil tests (imbibition), and the oil saturation decreased during the gas/oil tests (drainage), so they found little hysteresis in the wetting-phase relative permeability. The two curves did not agree for intermediate or oil-wet systems. Geffen *et al.*²⁸ compared steady-state gas/brine and oil/brine relative permeability ratios and found that they agreed in a strongly water-wet Alundum core.

Schneider and Owens⁵² compared steady-state oil/water relative permeabilities in a water-wet Torpedo sandstone core for increasing oil saturation (drainage) and increasing water saturation (imbibition). They found essentially no hysteresis in the water (wetting-phase) relative permeability. In a second set of experiments, Schneider and Owens⁵³ measured steady-state oil/water relative permeabilities on native-state San Andres and Grayburg cores, which are oil-wet as shown by contact-angle measurements. Starting at the initial water saturation, steady-state oil/water relative permeabilities with water saturation increasing (drainage in an oil-wet core) were followed by steady-state oil/water relative permeabilities with the water saturation decreasing (imbibition). In one plug, there was essentially no hysteresis in the oil (wetting-phase) relative permeability. Two other plugs showed some hysteresis in the oil relative permeability, although it is possible that the plugs were not strongly oil-wet.

McCaffery,⁴⁹ McCaffery and Bennion,⁵⁰ and Morrow and McCaffery⁵⁴ found essentially no hysteresis in the wetting-phase relative permeability when the wetting was sufficiently strong. They measured steady-state relative permeabilities in a teflon core with nitrogen as the nonwetting phase and heptane ($\theta = 20^\circ$ [0.35 rad]) or dodecane ($\theta = 42^\circ$ [0.73 rad]) as the wetting phase. They found that the wetting-phase relative permeability was not dependent on the prior saturation history or the direction of displacement. (These experiments, shown in Figs. 6 and 7, are discussed in more detail later.)

The experiments discussed above, which showed little or no relative permeability hysteresis in the wetting phase, used steady-state methods to determine oil/water relative permeability. Amaefule and Handy⁵⁵ measured steady-state imbibition and drainage relative permeabilities using brine and a refined oil in a fired, strongly water-wet Berea core, and found some hysteresis in the water relative permeability. Recently, several unsteady-state relative permeability measurements have shown significant hysteresis in the wetting-

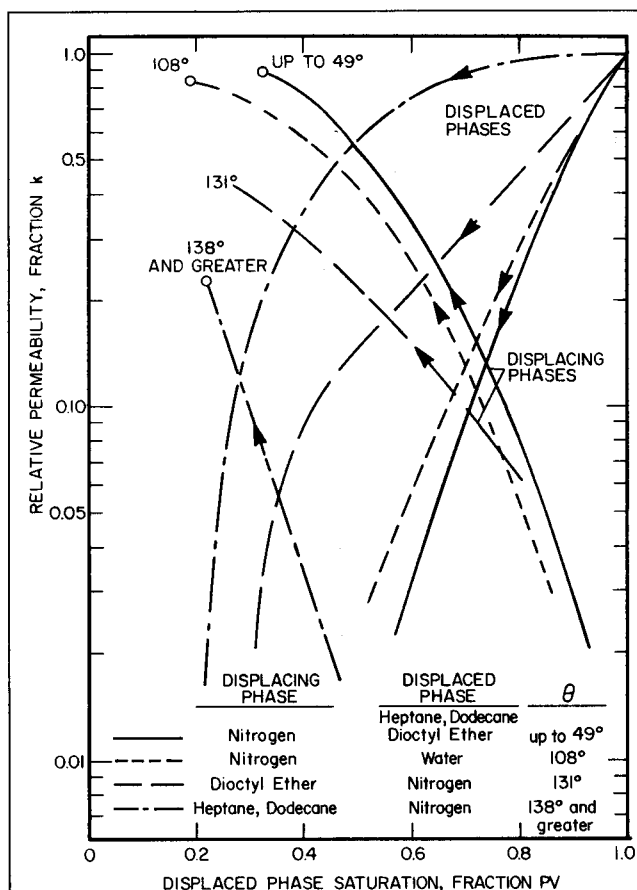


Fig. 6—Effect of wettability on relative permeability—artificial teflon plug, nitrogen, and pure fluids. Relative permeabilities are normalized with the absolute permeability. The plug was initially 100% saturated with the displaced phase. The contact angle, θ , was measured through the displaced phase on a smooth, flat plate. (From McCaffery.⁴⁹)

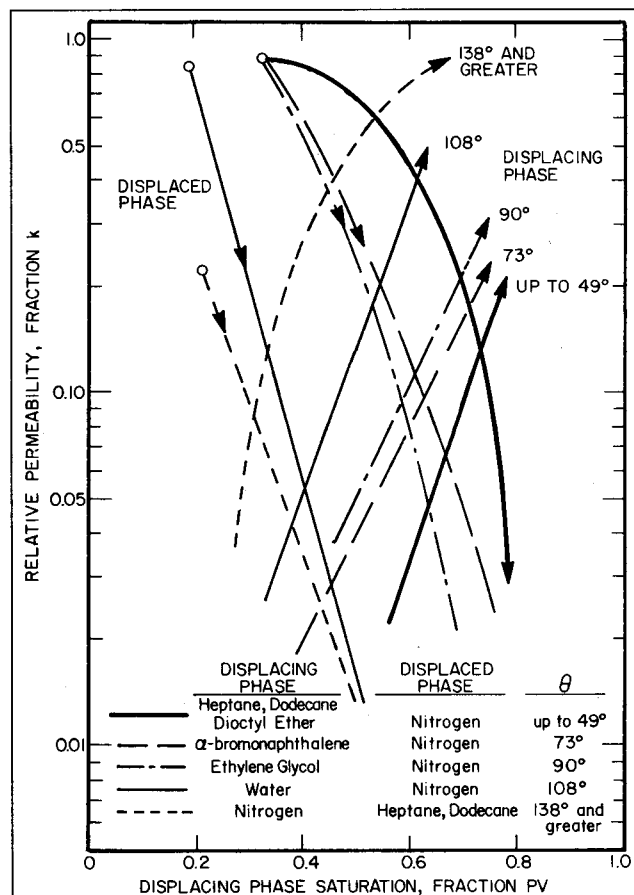


Fig. 7—Effect of wettability on relative permeability—artificial teflon plug, nitrogen, and pure fluids. The saturation of the displacing phase was initially at the irreducible value. The contact angle, θ , is measured through the displacing phase. (From McCaffery.⁴⁹)

phase relative permeability. Jones and Roszelle⁵⁶ and Sigmund and McCaffery⁵⁷ measured drainage and imbibition relative permeabilities in water-wet plugs. In both experiments, the plugs were initially at the IWS. The core was waterflooded, and the imbibition relative permeabilities (wetting phase increasing) were calculated from the pressure drop and production data. After the ROS was reached, the core was oilflooded and the drainage relative permeabilities were calculated. Both experiments found significant hysteresis in the wetting-phase (water) relative permeabilities, but very little hysteresis in the nonwetting-phase (oil) relative permeabilities. The reason for this discrepancy is not known. Craig⁶ and other researchers believe that problems occur with unsteady-state relative permeability measurements in strongly wetted systems with the wetting-phase saturation increasing (i.e., calculating unsteady-state relative permeabilities from a waterflood in a strongly water-wet system).

Effects of Wettability on Relative Permeability. The experiments discussed below examine the effects of wettability on relative permeability using cores with two different types of surfaces: uniform and heterogeneous. In uniformly wetted systems, the wettability of the entire surface is varied from water-wet to oil-wet, while attempting to keep the wettability of the entire surface as uniform as possible. Additional wettability effects will occur if the core has fractional or mixed wettability, where portions of the rock surfaces are water-wet but the remainder are oil-wet.

Relative permeability curves can be normalized with either (1) the absolute permeability of the core saturated with a single phase, usually brine or air, or (2) the effective permeability of the core at a specified initial saturation, such as the oil permeability at IWS. Although the absolute permeability is not affected by the wettability,

TABLE 2—EFFECTIVE OIL PERMEABILITIES AT AN INITIAL WATER SATURATION OF 20% AS A FUNCTION OF CONTACT ANGLE
Taken from Owens and Archer⁵¹

Effective Oil Permeability (md)	Contact Angle (degrees)
571	Air permeability
561	0—water-wet
472	47
459	90
380	138
357	180—oil-wet

the effective oil permeability at IWS decreases as a core becomes more oil-wet. An example is given in Table 2, taken from Owens and Archer.⁵¹ The choice of normalizing permeability affects how the shape of the plotted relative permeability curves will change as the wettability changes. As shown in Fig. 4, relative permeability curves normalized with the absolute permeability explicitly show the decline in relative (effective) oil permeability as the core becomes more oil-wet.¹⁹ On the other hand, relative permeability curves normalized with the effective oil permeability have already factored out this wettability effect; hence, all the curves will start at the same point, even though the wettability is changed (see Fig. 8).

Uniformly Wetted Systems

Fig. 8, taken from Owens and Archer,⁵¹ shows the effects of wettability on relative permeability measured with the Penn State steady-

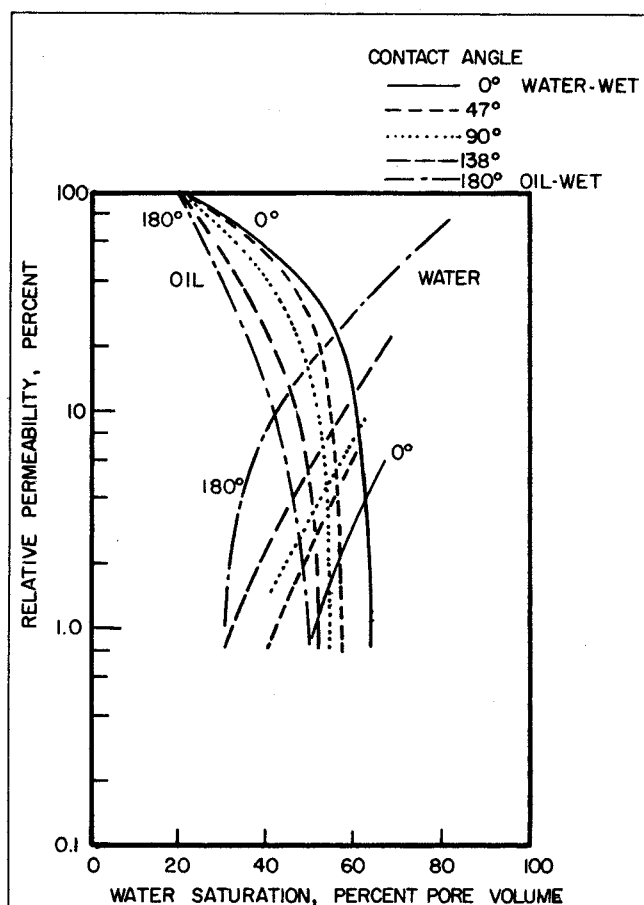


Fig. 8—Effects of wettability on relative permeability—outcrop Torpedo sandstone, brine, and BDNS-treated mineral oil. The contact angle, θ , was measured through the water. Relative permeabilities are based on the effective oil permeability at the initial water saturation. (From Owens and Archer.⁵¹)

state method. A mild NaCl brine and a 1.7-cp [1.7-mPa·s] refined mineral oil were used in an outcrop Torpedo sandstone that was fired before the experiments to stabilize clay minerals. The wettability of the system was controlled by adding either (1) various amounts of barium dinonyl-naphthalene sulfonate (BDNS) to the refined mineral oil, which made the system more oil-wet, or (2) Orvus K liquid (a detergent) to the brine to achieve a strongly water-wet system with a 0° contact angle through the brine. Wettability was monitored by contact-angle measurements on a quartz crystal. All the relative permeability tests started at an initial water saturation of about 20%. This was achieved by saturating the dry core with brine, then flooding it with a viscous mineral oil to the initial water saturation. Finally, the viscous mineral oil was replaced with the 1.7-cp [1.7-mPa·s] refined mineral oil containing the desired amounts of detergent or BDNS.

Fig. 8 shows that at any given water saturation, the water relative permeability increases as the system becomes more oil-wet. The oil relative permeability simultaneously decreases, causing a

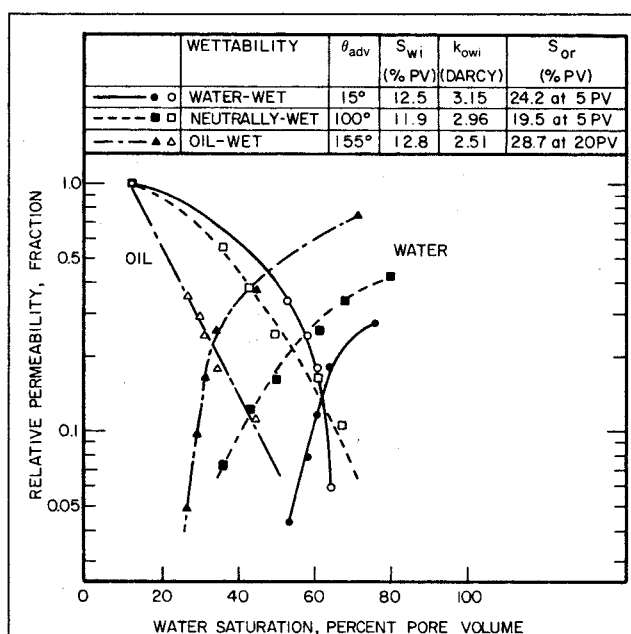


Fig. 9—Effects of wettability on relative permeability—dolomite pack, water, and oil treated with octanoic acid. Relative permeabilities are normalized with the effective oil permeability at the initial water saturation. (From Morrow et al.⁶²)

gradual reduction in the waterflooding efficiency. Owens and Archer normalized their curves with the effective oil permeability at the initial water saturation (see Table 2). The effective oil permeability decreases as the wettability is varied from water-wet to oil-wet. At a contact angle of 0° (measured through the water), the water has only a small influence on the effective oil permeability, which is almost equal to the absolute (air) permeability. The reason is that the initial 20% water saturation in the water-wet core is close to the IWS. At this condition, the water is present in the smallest pores and as a thin film on the rock surfaces, allowing the oil to flow through the larger pores. At 180° [3.14 rad] contact angle, water will be present in the form of blobs that can block the pore throats of the larger pores, substantially reducing the effective oil permeability.

Fig. 4 shows the results from unsteady-state relative permeabilities run in outcrop Torpedo sandstone cores using crude oil and brine and calculated by the Johnson-Bossler-Naumann⁵⁸ (JBN) method. Wettability was varied by treating the cores with different concentrations of organochlorosilanes and monitored with the U.S. Bureau of Mines (USBM) wettability method, where +1 indicates a strongly water-wet core, -1 a strongly oil-wet core, and 0 a neutrally wet core (see Table 3).^{2,59-61} The relative permeability curves are based on the absolute water permeability at 100% brine saturation. As the core becomes more oil-wet, the relative oil permeability decreases and the relative water permeability increases. However, in contrast to Fig. 8, which was normalized with the effective oil permeability, this set of curves shows how the oil permeability at the initial water saturation also decreases.

TABLE 3—APPROXIMATE RELATIONSHIP BETWEEN WETTABILITY, CONTACT ANGLE, AND THE USBM AND AMOTT WETTABILITY INDICES

	Water-Wet	Neutrally Wet	Oil-Wet
Contact Angle, degrees			
Minimum	0	60 to 75	105 to 120
Maximum	60 to 75	105 to 120	180
USBM Wettability Index	Near 1	Near 0	Near -1
Amott Wettability Index			
Displacement-by-water ratio	Positive	Zero	Zero
Displacement-by-oil ratio	Zero	Zero	Positive

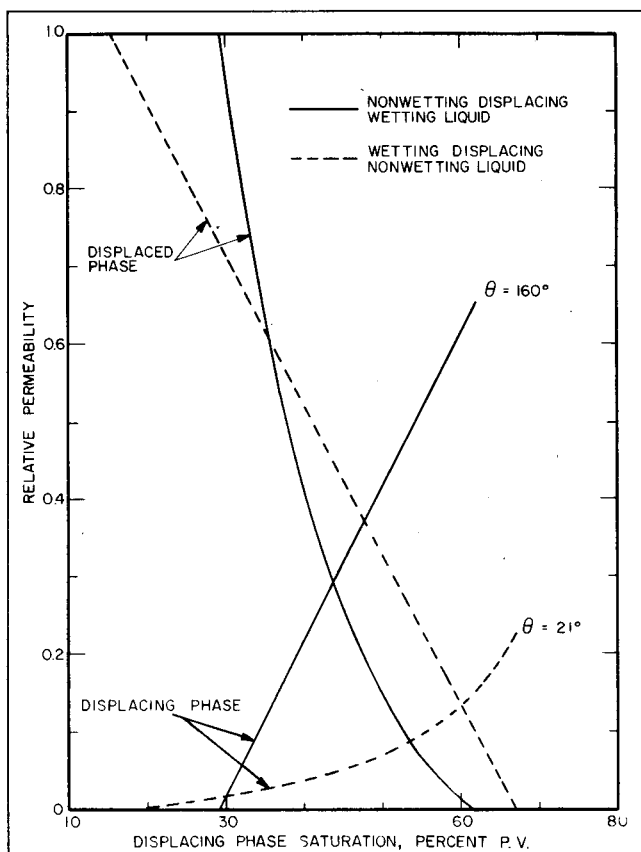


Fig. 10—Effect of wettability on relative permeability—sintered teflon core, refined mineral oil, and water or a sucrose solution. The contact angle, θ , is measured through the displacing phase on a flat teflon plate. (From Mungan.⁶³)

Morrow *et al.*⁶² measured steady-state relative permeabilities with water and a refined mineral oil, using packings of powdered dolomite as the porous medium. Wettability was controlled with different concentrations of octanoic acid in the oil. Water-advancing contact angles were measured on a smooth dolomite crystal. Relative permeabilities were measured at three different wettabilities: (1) water-wet, $\theta_{adv} = 15^\circ$ [0.26 rad], (2) neutrally wet, $\theta_{adv} = 100^\circ$ [1.75 rad], and (3) oil-wet, $\theta_{adv} = 155^\circ$ [2.7 rad]. All three tests started with initial water saturations of $12 \pm 1\%$ PV. The results are shown in Fig. 9, normalized with the effective oil permeability at the initial water saturation, which was 20% less for the oil-wet case than for the water-wet one. As the system becomes more oil-wet, the water relative permeability increases, while the oil relative permeability decreases. The crossover point, where the two relative permeabilities are equal, occurs at lower water saturations. The final water permeabilities at ROS of the water-wet and neutrally wet systems were measured after flowing 5 PV of brine through the system, after which no more oil was produced. For the oil-wet core, after 20 PV of brine were injected, a small amount of oil was still being produced. As discussed in more detail in Ref. 5, ROS's in oil-wet systems are less well defined when compared with water-wet systems.

Several researchers^{49,50,54,63,64} have used polytetrafluoroethylene (teflon) cores and pure fluids without surfactants to study the effects of wettability on relative permeability. The advantages of teflon are that it is chemically inert and has a low surface energy, allowing a wide range of contact angles to be obtained with various pairs of pure fluids that do not contain surfactants. The uniform composition of the core and the absence of surfactants combine to give a constant, uniform, and reproducible wettability, avoiding problems with nonuniform wettability or possible wettability alteration during the experiments.¹ The wettability of the teflon/fluid system is determined by contact-angle measurements on smooth

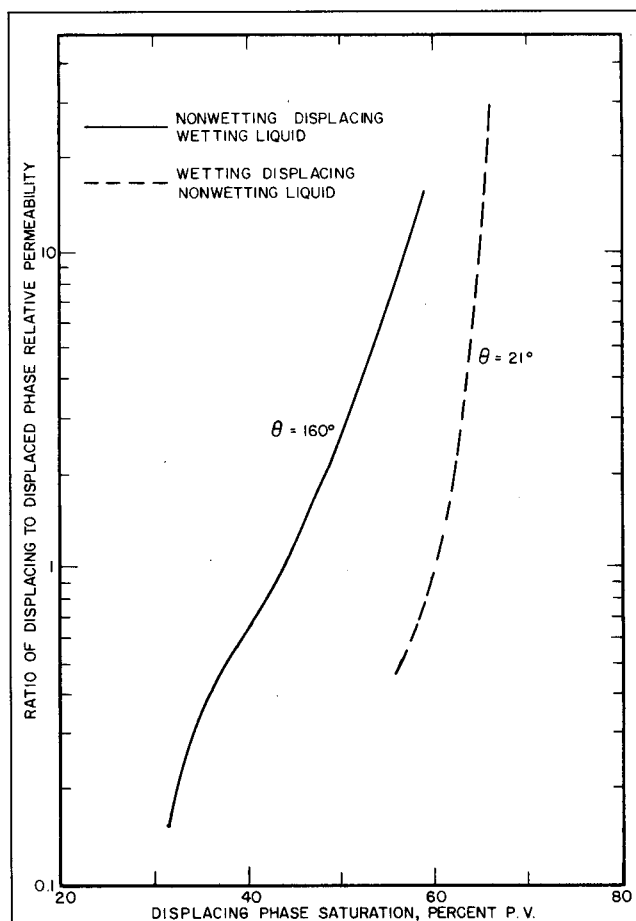


Fig. 11—Effect of wettability on relative permeability ratio—sintered teflon core, refined mineral oil, and water or a sucrose solution. (From Mungan.⁶³)

teflon plates. The advancing and receding contact angles are essentially equal because the measured contact angle generally has little or no hysteresis.

Stegemeier and Jessen⁶⁴ measured gas/liquid relative permeabilities using nitrogen and pure fluids in a teflon particle pack. The changes in relative permeability as the liquid phase became less wetting are consistent with the experiments discussed earlier. However, the changes are relatively small, possibly because of the homogeneous nature and high permeability (16 darcies) of the teflon pack.

Mungan⁶³ measured unsteady-state relative permeabilities in a sintered, consolidated teflon core with oil as the wetting fluid. A refined mineral oil and water or a sucrose solution were used, where the viscosity ratio was maintained constant by varying the sucrose concentration in the water. Typical results are shown in Fig. 10. For the wetting/displacing/nonwetting case (oilflood), the core was saturated with oil, driven to the ROS with sucrose solution, then oilflooded. Relative permeabilities were calculated by the JBN method and normalized with the water relative permeability at ROS. A similar procedure was used for the nonwetting/displacing/wetting case (waterflood). The contact angle was measured through the displacing phase on a smooth teflon plate. The changes in relative permeability for the two displacements are consistent with the other experiments discussed earlier. When the wetting fluid displaces the nonwetting one, the crossover point occurs at a higher displacing-phase saturation, and the displacing-phase relative permeability at floodout is lower.

Mungan also calculated relative permeability ratios, shown in Fig. 11. When the wetting fluid displaces the nonwetting one, the relative permeability ratio (displacing to the displaced phase) is nearly vertical and extends over a relatively short saturation interval. In contrast, when the nonwetting fluid displaces the wetting one, the relative permeability ratio is higher at a given saturation and ex-

tends over a greater saturation range. In reservoir systems, the slope of the relative permeability ratio (k_w/k_o) vs. S_w curve can sometimes be used as a qualitative indicator of the wettability.¹⁰ If the entire curve is nearly vertical and extends over a small saturation interval, the rock is strongly water-wet. Conversely, the rock is oil-wet if the ratio has a gentle slope and extends over a larger saturation interval. Note that while the relative permeability ratios in Fig. 9 do not cross, they may cross at very high relative permeability ratios if the oil-wet system has a lower ROS (e.g., see Raza *et al.*¹⁰).

McCaffery,⁴⁹ McCaffery and Bennion,⁵⁰ and Morrow and McCaffery⁵⁴ studied the effects of wettability on steady-state relative permeabilities using sintered teflon cores and various pairs of pure fluids (nitrogen and liquids). The first set of tests, shown in Fig. 6,⁴⁹ were primary drainage and imbibition tests. The core was initially saturated with one of the fluids, which will be referred to as the "displaced" liquid. The contact angle, measured through this displaced phase, ranged from 20° [0.35 rad] (nitrogen displacing heptane) to 160° [2.8 rad] (heptane displacing nitrogen). Steady-state relative permeabilities were measured at a series of decreasing saturations of the displaced phase, starting from 100% saturation. Primary-drainage relative permeabilities were measured when the contact angle through the displaced phase was less than 90° [1.57 rad], and primary imbibition measurements were made when the contact angle was greater than 90° [1.57 rad].

For example, one set of primary-drainage relative permeabilities was measured for nitrogen displacing dodecane. The teflon core was first saturated with dodecane; then the absolute permeability was measured with 100% dodecane flowing. Relative permeabilities were subsequently measured by increasing the flow rate of nitrogen and decreasing the flow rate of dodecane in a series of steps, while measuring saturation and pressure drop. During the final measurement, only nitrogen is flowing at the irreducible dodecane saturation. The reverse set of measurements, with dodecane displacing nitrogen from an initially 100% nitrogen-saturated core, were also made. These measurements were primary-imbibition relative permeabilities.

In Fig. 6, the relative permeabilities are normalized with the absolute permeability. The results are plotted vs. the displaced-phase saturation, and the contact angle was measured through the displaced phase on a flat teflon plate. As the contact angle increases and the displaced phase becomes less wetting, the displaced-phase relative permeability increases and the displacing-phase relative permeability decreases. The set of relative permeability curves marked "Up to 49°" are for a nonwetting fluid (nitrogen) displacing a wetting fluid (heptane, dodecane, or dioctyl ether) from the core. McCaffery and coworkers found essentially no effect of contact angle on relative permeability when one of the fluids wet the core strongly enough. The nitrogen (nonwetting phase) relative permeability at the irreducible wetting-phase saturation is high, roughly 90% of the absolute permeability. The relative permeability curves for a contact angle of 49° [0.86 rad] or less are analogous to water/oil relative permeability curves measured in a strongly oil-wet core, with the water saturation increasing. Comparing these curves with Figs. 2 and 3, we can see that the behavior is qualitatively similar. (Note that the curves are reversed because McCaffery's curves are plotted vs. displaced-phase saturation.)

As the displaced phase becomes less strongly wetting, its relative permeability increases while the relative permeability of the displacing phase decreases, as shown by the shift in the relative permeability curves for nitrogen displacing water ($\theta = 108^\circ$ [1.88 rad]) and dioctyl ether displacing nitrogen ($\theta = 131^\circ$ [2.29 rad]). The curves marked "138° and Greater" are for a wetting fluid (heptane or dodecane) displacing a nonwetting fluid (nitrogen). Again, McCaffery and coworkers found no effect of contact angle on relative permeability when the wetting is strong enough. These relative permeability curves are analogous to water/oil relative permeability curves measured in a strongly water-wet core, with the water saturation increasing. The wetting-phase relative permeability at the residual nonwetting-phase saturation is low, about 25% of the initial permeability, and the crossover point has shifted.

At the end of the steady-state relative permeability tests shown in Fig. 6, the core was left with an irreducible saturation of the

displaced phase in the core. McCaffery and coworkers then made a second set of steady-state relative permeability tests starting from this irreducible saturation. For example, in the first set of tests, nitrogen displaced dodecane from an initially 100% dodecane-saturated core in a series of steps, until only nitrogen was flowing at an irreducible dodecane saturation (primary drainage). During the second set of measurements, the nitrogen flow was decreased and the dodecane flow was increased in a series of steps, until finally only dodecane was flowing at an irreducible nitrogen saturation (secondary-imbibition measurements for this pair of fluids).

The results are shown in Fig. 7, normalized with the absolute permeability.⁴⁹ Note that the results are plotted vs. the displacing-phase saturation and the contact angle is measured through the displacing phase. This is done so that the two sets of relative permeability measurements in Figs. 6 and 7 can be compared easily, because the displaced and displacing phases have now been reversed. As the wetting tendency of a phase increases, its relative permeability decreases. In Fig. 7, for example, the relative permeability of the displaced phase decreases as the contact angle drops from 138° to 49° [2.4 to 0.86 rad]. However, as with the initially 100%-saturated measurements, McCaffery and coworkers found little effect of contact angle on wettability when the wetting was sufficiently strong. The curves marked "Up to 49°" are for a wetting phase (heptane, dodecane, or dioctyl ether) displacing a nonwetting phase (nitrogen), with a low relative permeability of the wetting phase at the nonwetting-phase residual saturation. Again, note the similarity to water/oil relative permeability curves measured in a water-wet core with water saturation increasing. As the wetting of the displacing phase gradually decreases, the curves shift, with the displacing-phase relative permeability increasing while the displaced-phase relative permeability decreases. The curve marked "138° and Greater" is for a strongly nonwetting phase (nitrogen) displacing a wetting phase (heptane, dodecane, or dioctyl ether) from the core. Note that these experiments start at different values of the irreducible saturation, in contrast to the work by Owens and Archer.⁵¹ The differences in starting saturation may also affect the relative permeability curves.⁴⁶

McCaffery and coworkers found essentially no hysteresis in the wetting-phase relative permeability when wetting was sufficiently strong. The relative permeability of heptane ($\theta = 20^\circ$ [0.35 rad]) or dodecane ($\theta = 42^\circ$ [0.73 rad]) measured with nitrogen as the second fluid was not dependent on prior saturation history or the direction of displacement. A comparison of the four heptane/dodecane curves ("Up to 49°" and "138° and Greater") in Figs. 6 and 7 shows that they are essentially identical. Two of the curves are reversed because heptane and dodecane were used as both displacing and displaced fluids in both figures.

These results are generally consistent with the other experiments discussed earlier.^{19,51,62} The most notable difference is that McCaffery and coworkers found that relative permeability is insensitive to changes in wettability and contact angle when the system is strongly wetted, with large changes occurring only when the system is near neutral wettability. Similarly, Morrow and McCaffery,⁵⁴ Morrow and Mungan,⁶³ and Morrow⁶⁶ found that capillary pressure curves measured in teflon plugs were also insensitive to changes in wettability when wetting was sufficiently strong. In contrast, Owens and Archer⁵¹ found changes in the relative permeability curves when the contact angle varied from 0° to 47° [0 to 0.82 rad] (see Fig. 8). The reason for this disagreement is unknown.

Effects of Core Cleaning and Handling

The experiments discussed above attempted to vary wettability systematically. In this section, we will review some experiments that show how core cleaning and handling can drastically affect relative permeability by altering the wettability of core. Note that some of these experiments were made on reservoir core, which may have nonuniform wettability.

Fig. 12, taken from Mungan,⁶⁷ shows native-state, cleaned, and restored-state relative permeabilities measured on a single core using the unsteady-state JBN⁵⁸ technique. All curves are based on the effective oil permeability at IWS. Native-state core was cut from a Pennsylvanian sandstone reservoir with lease crude oil, then stored

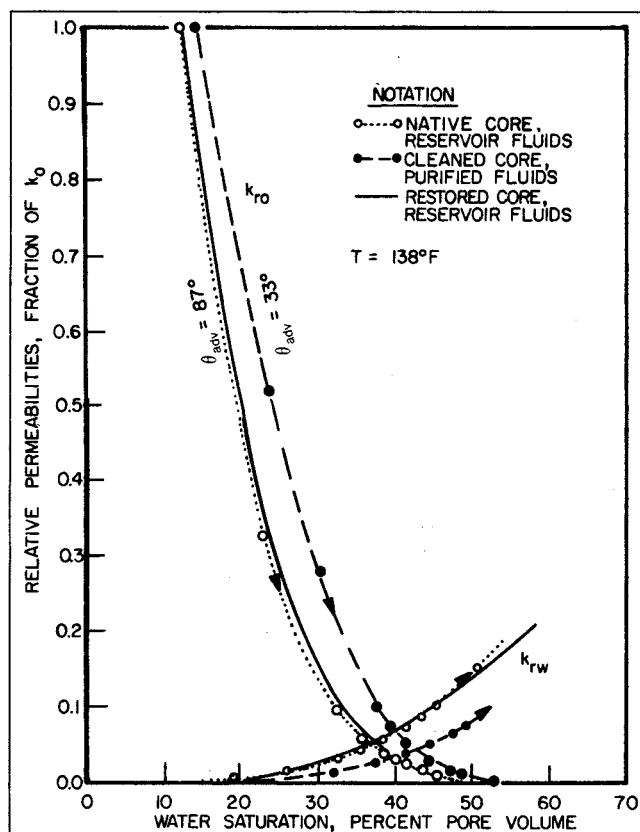


Fig. 12—Effect of wettability on relative permeability with a reservoir core in the native, cleaned, and restored states. The advancing contact angle, θ_{adv} , measured on a flat quartz surface, was 87° for the reservoir fluids and 33° for brine and the refined oil. (From Mungan.⁶⁷)

in lease crude to preserve wettability. Relative permeability was measured on the native-state core with brine and live crude oil at reservoir temperature (138°F [59°C]) and a pressure high enough to keep all gases in solution. The core was cleaned with benzene, followed by toluene, and then dried. Relative permeabilities were remeasured on the cleaned core using synthetic formation brine and a refined oil. Based on Craig's rules of thumb for wettability (see Table 1), the cleaned core is significantly more water-wet than the native-state one. This is confirmed by contact-angle measurements. The water-advancing contact angle, θ_{adv} , was 33° [0.58 rad] for the refined oil and brine and 87° [1.52 rad] for live reservoir fluids on a quartz surface. Finally, the cleaned core was saturated with brine, driven to IWS with crude, and aged at the reservoir temperature for 6 days to restore wettability. The relative permeability for the core in the restored state was then measured. Fig. 12 shows that it is very similar to the native-state relative permeability, implying that the wettability was successfully restored. Mungan then repeated the cleaning, restoration, and relative permeability measurements on the same core and obtained identical results.

Mungan's experiments show the importance of measuring relative permeability on native-state or restored-state cores, rather than on cleaned ones. At any water saturation, the relative oil permeabilities were lower and the relative water permeabilities were higher for the native- and restored-state core when compared with the more water-wet cleaned core. If a cleaned core were used to predict water-flood behavior, it would predict higher recovery efficiencies and later breakthrough than the actual behavior. Similar results comparing native-state vs. cleaned relative permeabilities can be found in Refs. 47, 68, and 69.

Wendel *et al.*⁷⁰ measured unsteady-state water/oil relative permeabilities on Hutton plugs in their contaminated, cleaned, and restored states (see Fig. 13). Contamination by surfactants in the invert-oil-emulsion mud used to drill the well rendered the cores

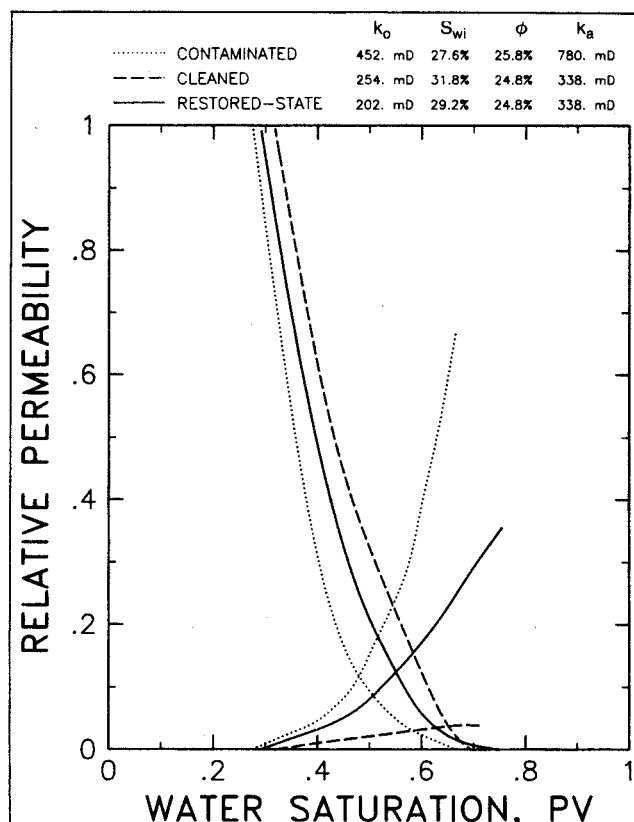


Fig. 13—Comparison of oil/water relative permeabilities measured on contaminated, cleaned, and restored-state plugs, Hutton massive sand zone: (1) contaminated, oil-wet plug, Well H3/21, 10,092 ft; (2) cleaned, strongly water-wet plug, Well H5/13, 10,077 ft; (3) restored-state measurements on the cleaned plug after saturation with formation fluids and aging. (From Wendel *et al.*⁷⁰)

oil-wet, as shown by relative permeability and USBM wettability measurements. Craig's rules of thumb (Table 1) show that the contaminated plug shown in Fig. 13 is strongly oil-wet. The crossover point for the oil and water relative permeabilities occurs at a water saturation of 48%, while the water relative permeability at floodout is about 67%. Wendel *et al.* were able to clean the cores and remove the drilling-mud surfactants using three successive Dean-Stark extractions with toluene, glacial acetic acid, and ethanol. In general, the cleaned cores were strongly water-wet. (Some cores could be cleaned only to neutral wettability, possibly because of the presence of coal, which is naturally neutrally wet.) Fig. 13 shows oil/water relative permeabilities measured on a second plug after cleaning, with a USBM wettability index of $+0.64$ after cleaning. The crossover point for the oil and water relative permeabilities occurs at a water saturation of 65% PV, while the water relative permeability at floodout is only 8%. Finally, Wendel *et al.* restored the wettability of the cleaned, water-wet cores by saturating the cores with formation fluids and aging the cores at reservoir temperature for 1,000 hours. The restored-state cores were neutrally wet, with relative permeability characteristics intermediate between measurements in the contaminated, strongly oil-wet state and the cleaned, strongly water-wet state. The restored-state relative permeabilities shown in Fig. 13 were measured on the cleaned plug after saturation and aging. The crossover point occurred at a water saturation of 56% PV, whereas the water relative permeability at floodout was 42%.

Keelan⁷¹ also compared unsteady-state oil/water relative permeabilities measured in a contaminated, oil-wet core vs. the same core after it had been cleaned and rendered strongly water-wet (see Fig. 14). Measurements were first made on an oil-wet, weathered core taken with wettability-altering chemicals in the mud. The core was then cleaned and rendered water-wet by firing at 572°F [300°C] in an oxygen/ CO_2 atmosphere to remove all adsorbed, wettability-

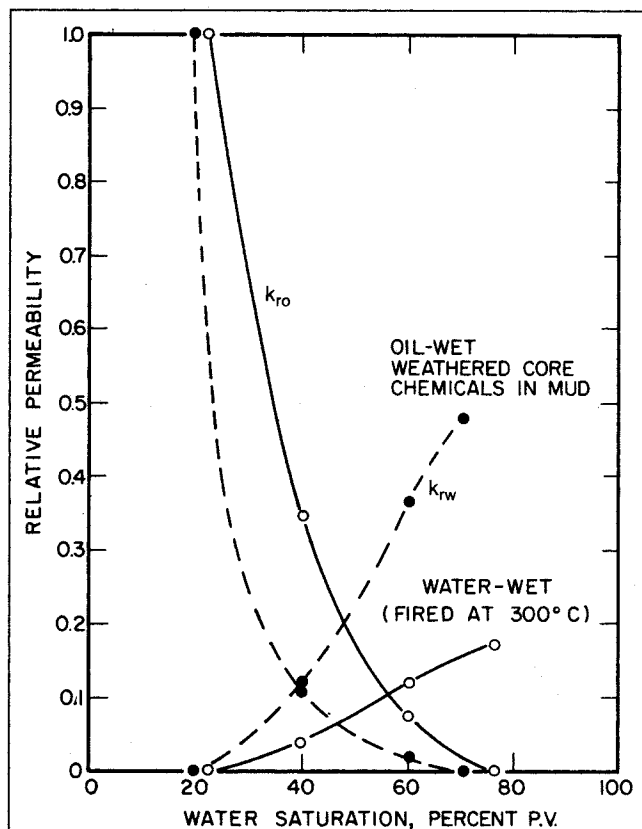


Fig. 14—Contaminated vs. cleaned oil/water relative permeabilities—sandstone plug. (From Keelan.⁷¹)

altering compounds. The changes in the relative permeability curves are similar to those observed by Wendel *et al.*

Wang⁶⁹ saturated a Berea core with brine, oilflooded it with dead Loudon crude, and then waterflooded it to ROS. The core was flushed with Loudon crude to IWS and allowed to age at 160°F [71°C] for 1 year before steady-state water/oil relative permeability was measured. The core was significantly less water-wet after aging. The ROS was initially 42.5% PV, but decreased to less than 17% PV after aging. Waterflood tests indicated that the aged core probably had mixed wettability.^{69,72} Wang compared the steady-state water/oil relative permeabilities of the aged Berea core with relative permeabilities measured without aging in an adjacent Berea core using brine and dead Loudon crude. According to Craig's rules of thumb, the unaged core was significantly more water-wet: (1) crossover saturation without aging was roughly 50% PV vs. 60% PV for the aged core; (2) water relative permeability at ROS for the unaged core was roughly 5% vs. 30% after aging; and (3) ROS without aging was roughly 47% PV vs. 17% PV for the aged core.

Grist *et al.*⁷³ showed how different cleaning methods could alter the effective permeability and wettability of cleaned cores. Similar cores were cleaned by several currently used methods and then waterflooded before the ROS and endpoint effective water permeability were measured. The ROS was very similar for all cleaning methods. However, the endpoint effective permeability varied by more than a factor of 3 between cleaning methods. Their explanation for this behavior was that some methods were able to extract more of the adsorbed, wettability-altering compounds, leaving the rock more water-wet. In the more water-wet cores, the residual oil had a greater tendency to form trapped droplets, blocking pore throats and lowering effective water permeability. The least effective of the three methods was an overnight reflux extraction with toluene. A reflux extraction with toluene followed by extraction with a mixture of chloroform and methanol for 2 days was more effective. Finally, the most effective method used reflux extrac-

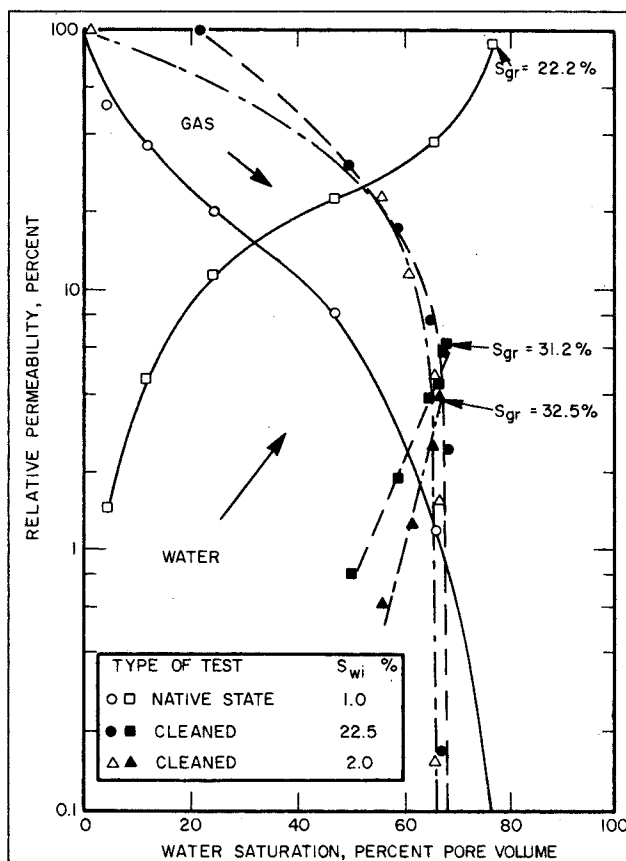


Fig. 15—Comparison of native-state and cleaned water/gas relative permeabilities—San Andres plug. $k_{gi} = 135$ md, $\phi = 20.3\%$. (From Schneider and Owens.⁵³)

tion with toluene followed by extraction with chloroform and methanol for 3 weeks. In the final stage of the cleaning, methanol alone was used.

Although the authors cited above have found that the cleaned cores were more water-wet, it is also possible for cleaning to change a core from water-wet to oil-wet, either by deposition of compounds from the oil⁷⁴ or by adsorption of the cleaning solvents.⁷⁵ In any case, cleaning the core can introduce serious errors in the relative permeability measurements.

Jennings⁷⁶ used toluene extraction to clean cores from different reservoirs and found that the wettabilities and relative permeabilities were not changed. The initial wettabilities of the cores before cleaning ranged from water-wet to oil-wet. Jennings stated that his results indicated that toluene-extracted cores retained the reservoir wettability and could be used for relative permeability measurements. In general, however, this is not the case, except for strongly water-wet reservoirs where there are no adsorbed wettability-altering compounds to be removed during cleaning. Although it is often less efficient than other solvents, toluene extraction can alter the wettability and relative permeabilities of a core.^{1,69,77} In some cases, we have found that neutrally wet or mildly oil-wet native-state core becomes strongly water-wet after extraction with toluene. The relative permeability curves also shift. Amott⁷⁷ has also found that toluene extraction can clean some cores, while it has little effect on others, such as the strongly oil-wet Bradford cores. Wang⁶⁹ found that extracting native-state Loudon cores with toluene made them more water-wet and altered the relative permeability curves. Therefore, since toluene extraction will alter the wettability and relative permeability of many native-state cores, measurements should be made on native-state cores before toluene extraction.

Based on recent work,^{70,75} it is possible that Jennings was not able to alter the wettability with toluene because many of his cores were taken with either oil-based or surfactant/emulsion drilling fluids. The surfactants in drilling muds, which can render core oil-wet, are very difficult to remove. For example, Wendel *et al.*⁷⁰

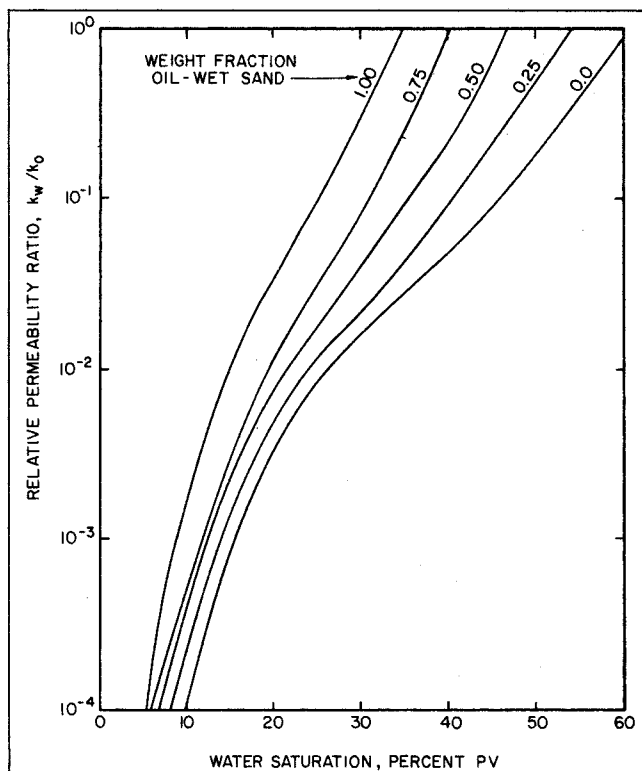


Fig. 16—Water/oil relative permeability ratio curves for fractionally wetted sandpacks. (From Fatt and Klirkoff.⁷⁹)

found that toluene extraction would not remove the surfactants deposited on Hutton core by an invert-oil-emulsion mud. It was necessary to remove the surfactants by three successive Dean-Stark extractions using toluene, glacial acetic acid, and ethanol.

Schneider and Owens⁵³ examined the effects of cleaning on steady-state, gas/water relative permeabilities measured in a San Andres carbonate core taken from an oil reservoir. Oil/water contact-angle measurements indicated that the reservoir was moderately oil-wet. The experiments were designed to study the late stages of a miscible flood. In a miscible flood, a gas such as CO₂ is injected into the reservoir to displace the oil, followed by water injection to displace the gas and oil. In areas swept by gas, the gas saturation is high and the water saturation is relatively low before water injection. The gas/water relative permeability curves measured in the direction of increasing water saturation are needed to predict the behavior of the injected water.

The native-state core used in the experiments was prepared by flushing with pentane under backpressure to remove the crude, followed by nitrogen to remove the pentane, leaving a core containing only brine and gas. It was assumed that this procedure did not significantly alter the wettability. Steady-state gas/water relative permeability was measured on the flushed, native-state core in the direction of increasing water saturation. The native-state gas/water relative permeabilities, shown in Fig. 15, indicate that the core is behaving as if it is oil-wet (more accurately, as if it is water-repellant, since the oil saturation is zero). The crossover point at which the gas and water relative permeabilities are equal occurs at a water saturation of about 30%. The water relative permeability at the residual gas saturation is more than 90% of the initial gas relative permeability. Note that the initial water saturation is only 1%, which is extremely low. It is not known whether the reservoir water saturation is this low or whether the water saturation was lowered during the pentane flush and subsequent evaporation of the pentane.

After native-state gas/water relative permeability measurements were made, the core was cleaned and dried, and gas/water relative permeabilities were measured on the cleaned core with two different initial water saturations. In the first set of measurements, an initial water saturation of 22.5% was established with a centrifuge technique. In the second set, a special low-salinity brine was used

TABLE 4—ROS AT WOR = 100, FRACTIONALLY WETTED SANDPACKS⁷⁹

Oil-wet Sand (%)	ROS (%)
0	28
25	35
50	40
75	45
100	48

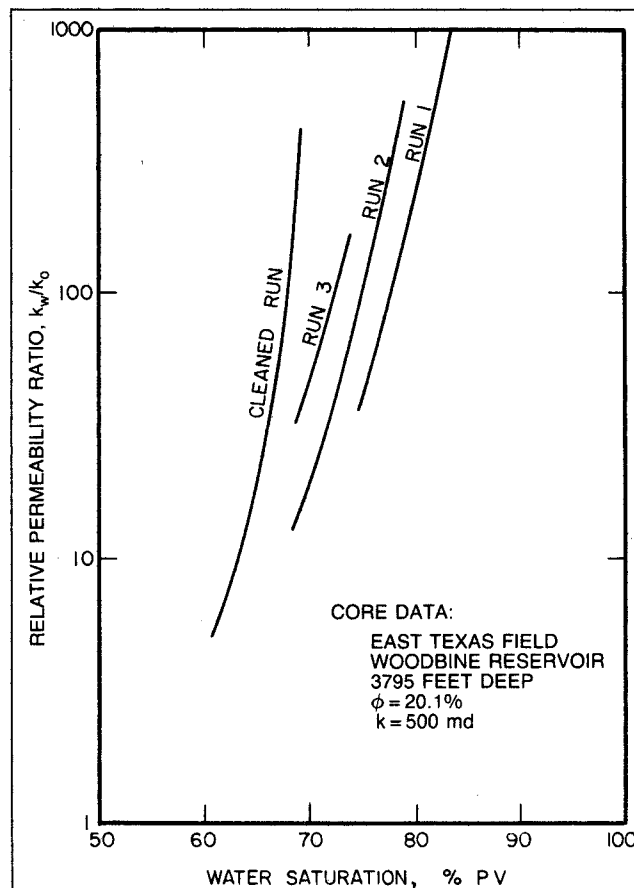


Fig. 17—Unsteady-state water/oil relative permeability ratios, k_w/k_o , measured during a series of waterfloods of a native-state East Texas Woodbine core that initially had a mixed wettability. (From Richardson et al.⁸⁴)

and dry nitrogen was injected to reduce the water saturation to 2%, in close agreement with the initial water saturation in the native-state test. The measurements, shown in Fig. 15, are completely different from the native-state ones. The residual gas saturation is higher and the water endpoint relative permeability is much lower at less than 10% of the initial permeability, indicating that the residual gas strongly interferes with the water flow. Based on their previous work, Schneider and Owens⁵² believe that the native-state core is oil-wet, while the cleaned core is water-wet. This is consistent with the gas/liquid relative permeability measurements made by McCaffery⁴⁹ and McCaffery and Bennion⁵⁰ (see Figs. 6 and 7). Schneider and Owens conclude that gas/water relative permeability data for tertiary oil recovery processes should be measured on native-state core, where the reservoir wettability is maintained.

In summary, the most accurate relative permeability measurements are made on native-state core, where the reservoir wettability is preserved. When such core is unavailable, restored-state core should be used, where the wettability is restored by a three-step process: (1) cleaning the core to remove all adsorbed compounds, (2) saturating with formation fluids, and (3) aging at reservoir conditions. Serious errors can result when measurements are made on

core with altered wettability, such as cleaned core or core contaminated with drilling-mud surfactants. For example, if the reservoir is oil-wet or intermediate-wet and a clean, water-wet core is used, the water relative permeability will be underestimated and the oil relative permeability will be overestimated. More water and less oil will flow at any given saturation than what the clean core would predict.

Fractional and Mixed-Wet Systems

In the experiments in uniformly wetted porous media, the wettability of the core was varied, while the wettability of the entire surface was kept as uniform as possible. For example, all the rock surfaces in a neutrally wet system should have little preference for oil or water. However, many reservoir rocks have heterogeneous wettability, with variations in wetting preference on different surfaces. Additional wettability effects will occur when the system has nonuniform wettability (either fractional or mixed) where portions of the surface are strongly water-wet, while the remainder is strongly oil-wet.^{1,72,78} Salathiel⁷² introduced the term "mixed" wettability for a special type of fractional wettability in which the oil-wet surfaces form continuous paths through the larger pores. The small pores remain water-wet, containing no oil. Note that the main distinction between mixed and fractional wettability is that the latter does not imply either specific locations for the oil-wet and water-wet surfaces or continuous oil-wet paths. In fractionally wetted systems, the individual water-wet and oil-wet surfaces have sizes on the order of a single pore.

Fractional Wettability. Fatt and Klikoff⁷⁹ measured the relative permeability ratio (k_w/k_o) in fractionally wetted sandpacks that were formed by mixing treated and untreated sand grains together. The untreated sand grains were strongly water-wet. The remaining sand grains were treated with Drifilm™, an organochlorosilane, to render them oil-wet. During mixing, some Drifilm may have been transferred to some of the water-wet sand grains, probably giving them a nonzero contact angle.⁷⁹ The absolute permeability of the sandpacks was roughly 3.2 darcies. The fractionally wetted sandpacks were saturated with water and then driven to IWS with a refined mineral oil.

Fig. 16 shows the relative permeability ratios calculated from constant-rate waterflood data by Welge's method.⁸⁰ The changes in the relative permeability ratio are similar to the changes observed when the wettability of a uniformly wetted core is changed from water-wet to oil-wet (see Fig. 11). In Fig. 11, the relative permeability ratio for the nonwetting fluid displacing the wetting fluid (analogous to a waterflood in an oil-wet core) is above the ratio for the reverse displacement. Similarly, in Fig. 16 the relative permeability ratio for waterflooding the oil-wet pack lies above the ratio for the water-wet one. The remaining curves lie between the two extremes. Fatt and Klikoff state that the relatively small difference in position of the curves for the 100% water-wet and 100% oil-wet sandpacks results from the relatively narrow pore-size distribution of the sandpack when compared with the pore-size distribution in reservoir sandstones. Table 4 gives the ROS measured at WOR=100. The oil recovery decreases as the system becomes more oil-wet.

Singhal *et al.*⁸¹ measured unsteady-state relative permeabilities in fractionally wetted bead packs where the fractional wettability was altered by changing the percentages of water-wet (glass) and oil-wet (teflon) beads. Distilled water and a series of refined organic liquids were used, which gave contact angles measured through the water that ranged from 40 to 77° [0.70 to 1.34 rad] for glass and 83 to 157° [1.45 to 2.74 rad] for the teflon. The glass was always the more strongly water-wet surface, while the teflon was always more oil-wet for all the fluid pairs used. The dry bead pack was first saturated by water, then flooded with an organic liquid to the residual water saturation. Relative permeabilities were calculated by the JBN method.⁵⁸ After cleaning, the dry bead pack was saturated with the organic liquid and waterflooded, and unsteady-state relative permeabilities were again calculated by the JBN method. The fact that the core was initially 100% saturated with the nonwetting fluid may have influenced the relative permeability.^{6,10,82,83}

Generally, Singhal *et al.* found that the ratio of relative permeability of the injected phase to the displaced phase, k_i/k_d , at a given injected-phase saturation increased as the fraction of surface wetted by the injected phase was decreased, although there were some exceptions. This is consistent with the behavior observed by Mungan⁶³ for uniformly wetted systems (Fig. 11), and by Fatt and Klikoff⁷⁹ for fractionally wetted systems (Fig. 16). Singhal *et al.* were not able to determine a definite trend in the individual oil (organic liquid) and water effective permeabilities at a given saturation as the wettability was altered. The scatter in their data probably resulted at least partly from changes in the pore-size distribution as the fractional wettability was altered. Unfortunately, the alterations in the wettability also changed the bead-size (and pore-size) distribution because the glass beads were roughly eight times larger in diameter than the teflon beads.

Mixed Wettability. Richardson *et al.*⁸⁴ measured unsteady-state oil/water relative permeabilities on native-state East Texas Woodbine cores. These cores were later shown by Salathiel⁷² to have mixed wettability, where continuous oil-wet paths in the larger pores allow oil drainage to occur until very low oil saturations are obtained after the injection of a very large number of PV's of water. The waterflood behavior is discussed in more detail in Ref. 5. Native-state Woodbine cores were oilflooded with kerosene until brine production stopped. The cores were then waterflooded and the relative permeability ratio was calculated. This procedure was repeated through several additional cycles of oilflooding followed by waterflooding. Finally, the cores were extracted with benzene and methanol, dried, saturated with brine, and then oilflooded. The relative permeability ratio of the cleaned core was then measured by waterflooding with brine.

Fig. 17, taken from Richardson *et al.*,⁸⁴ shows the changes in the relationship between water saturation and relative permeability ratio, k_w/k_o , as a core was repeatedly oilflooded and waterflooded. Run 1, the initial waterflood of the native-state core, had a very low ROS. Note that substantial oil is produced at very high water/oil ratios. ROS averaged about 12% PV for the nine native-state samples tested after the injection of roughly 40 PV of water.^{72,84} Three of the cores had very low ROS's, on the order of 2% PV. During the repeated cycles of oilflooding followed by waterflooding, the water/oil relative permeability ratio increased for a given water saturation (see Runs 2 and 3 in Fig. 17). In addition, the ROS increased. The relative permeability ratio for the extracted core increased even more, with an average ROS after extraction of 30% PV. Imbibition tests showed that the cleaned core was more water-wet than the native-state core because it imbibed water more rapidly.

The behavior of the relative permeability ratio as the core was cleaned and rendered water-wet contrasts with the behavior for uniformly and fractionally wetted systems (see Figs. 11 and 16). In these cases, the relative permeability ratio at a given water saturation was lowest for a strongly water-wet system (wetting fluid displacing nonwetting fluid), and the more oil-wet curves were to the left of the strongly wet curve. In Fig. 17, the water-wet curve lies to the left of the native-state curve. This behavior occurs because the native-state core has mixed wettability.

At the same time that the residual oil was increasing during the repeated floods, the IWS was decreasing. The native-state core generally had a high IWS after the first oilflood, with an average value of 40% PV. After the second oilflood, the average IWS decreased to 34% PV. After cleaning, the IWS was only 20% PV. The changes in the relative permeabilities, IWS, and ROS during the repeated oil- and waterflooding before cleaning are probably caused either by hysteresis effects or by alterations in wettability. Richardson *et al.* found similar increases in the ROS when a second set of native-state plugs was exposed to oxygen during storage. In many cases, oxidation of crude has been shown to alter wettability.¹ Cores were stored under four different procedures: (1) wrapped in metal foil and sealed in paraffin; (2) stored in deaerated formation brine; (3) stored in aerated formation brine; and (4) stored in cloth core bags. Samples were flooded to IWS with kerosene and then waterflooded. The ROS of cores stored by the first two methods was about 13%, while cores stored by the sec-

ond two methods (and exposed to oxygen) had ROS's of roughly 25%.

Burkhardt *et al.*⁸⁵ also made unsteady-state relative permeability measurements on preserved East Texas Woodbine plugs and compared them with relative permeability measurements on the same plugs after they had been cleaned and rendered water-wet. Burkhardt *et al.* also found a significant shift in the relative permeability ratio after cleaning. At low relative permeability ratios, the preserved-state relative permeability ratio was higher at a given water saturation. It appears that the two curves would cross at higher relative permeability ratios (higher water saturations), with a lower ROS for the preserved plugs. This would be consistent with Richardson *et al.*'s results (see Fig. 17). Unfortunately, Burkhardt *et al.* did not waterflood the plugs to very high water/oil ratios. In addition, the plugs were sealed with aluminum foil and paraffin, then stored for 3½ years before testing. It is possible that some wettability alteration occurred during this time, either from oxidation of the crude or evaporation of the brine and crude.

Unsteady-State Relative Permeability

Relative permeabilities can be measured either by steady- or unsteady-state methods.^{7,86} In the various steady-state methods, oil and water are injected at constant rates into the core until the saturations reach equilibrium values. The pressure drop across the core is then measured to determine the relative permeabilities. The main difference in the various steady-state methods is the procedure used to minimize outlet end effects. Steady-state methods are generally very slow, taking days or weeks, because the saturations must reach equilibrium after each change in the injection flow rates. The unsteady-state (external-drive) method is much more rapid, requiring only hours to determine the entire relative permeability curve, and for this reason it is usually used. A core is first flooded with oil and driven to IWS. Water is then injected into the core at a steady rate, and the relative permeability is calculated from the pressure drop and produced fluids using the JBN method.^{58,80,87} Viscous oils are normally used to increase the period of two-phase production, because the flow before breakthrough gives no information about the relative permeability. If low-viscosity oils are used in a water-wet core, the displacement is pistonlike and the relative permeabilities can be found only for the IWS and ROS using the unsteady-state method.⁸⁸

Craig⁶ and others^{10,89-91} recommend that the unsteady-state method not be used with strongly water-wet cores. They believe that the combination of high velocities and high viscosities that are commonly used in the unsteady-state measurements will cause a strongly water-wet core to behave as if it were oil-wet during a waterflood because of insufficient time for the fluids to come to equilibrium. Note that they are not referring to the increased two-phase production after breakthrough with a higher-viscosity oil, but instead to changes in the calculated relative permeability curves.

When a waterflood is conducted at a sufficiently slow rate with a low-viscosity oil, the distribution of the oil in the pores will change as the waterfront passes. If the system is strongly water-wet, the water will displace the oil from the smaller pores and the pore surfaces. However, Craig⁶ states that the water wetness of the core will be masked when viscous oils and high displacement rates are used because the viscous oil will not have enough time to adjust to the waterflood. The high rates are necessary to stabilize the flow and to minimize outlet end effects.^{6,92} The injected water will tend to move rapidly through the larger pores, causing early breakthrough and making the waterflood behave as if the core were oil-wet. In comparison with steady-state relative permeabilities, the calculated unsteady-state relative permeabilities will also appear more oil-wet (see Table 1).⁶

Unsteady-state relative permeabilities will appear more oil-wet when measurements are made on strongly water-wet systems initially 100% saturated with oil.^{82,93} Newcombe *et al.*⁸³ waterflooded water-wet sandpacks initially 100% saturated with a 1.3-cp [1.3-mPa·s] refined mineral oil and obtained significant amounts of simultaneous oil and water production after breakthrough. Generally, there is little or no production after water breakthrough in a strongly water-wet core with a low oil/water viscosity ratio, so this core behaved as if it were somewhat oil-wet.^{6,10,51,59,94} Leach *et*

*al.*⁸² pointed out that this behavior was caused by a lack of wetting equilibrium during the waterflood. During a waterflood of a water-wet, initially 100% oil-saturated core, water will displace oil from the pore surfaces. However, achieving wetting equilibrium is a relatively slow process. If water is injected at too high a rate, wetting equilibrium will not be achieved and the system will appear more oil-wet. Leach *et al.* presented results comparing the effects of water injection rate on ROS in water-wet packs with and without an initial water saturation. They found that the apparent oil-wetness of packs without an initial water saturation increased as the water injection rate increased.

Unfortunately, there are very few data in the literature either to prove or to disprove the hypothesis for strongly water-wet systems initially at the IWS, where the system should be in wetting equilibrium. Most of the early work comparing the steady- and unsteady-state methods used either gas drives, where oil was the wetting fluid, or cores that were treated to make them oil-wet. In both cases, the nonwetting fluid displaces the wetting fluid (drainage) during the measurement. In addition, much of the work used sandpacks, which have a fairly uniform pore-size distribution. The effect of viscosity and flow rate on the trapping of residual oil is probably much less important in these homogeneous packs than in consolidated cores.⁹⁵

Johnson *et al.*⁵⁸ compared steady- and unsteady-state oil/water relative permeabilities in a Weiler sandstone and found good agreement. The plug was initially at IWS and appears to have been strongly water-wet. Unfortunately, the viscosity of the oil is not given. Amaefule and Handy,⁵⁵ however, found significant differences between steady- and unsteady-state imbibition relative permeabilities in a fired, strongly water-wet Berea core with the low oil/water viscosity ratio of 1.28. The unsteady-state relative permeabilities appeared to be more oil-wet than the steady-state ones, which supports Craig's hypothesis. In the unsteady-state runs, the crossover point of the water and oil relative permeability curves shifted toward lower water saturations. In addition, the unsteady-state water relative permeabilities were higher than the steady-state water permeabilities at the same water saturation. As shown in Table 1, this indicates that the unsteady-state relative permeabilities acted more oil-wet. Another factor indicating differences in steady- and unsteady-state relative permeabilities is the difference in hysteresis in the wetting phase during drainage and imbibition. As discussed earlier, many steady-state measurements show little or no hysteresis in the wetting-phase relative permeability, while unsteady-state experiments by Jones and Roszelle⁵⁶ and Sigmund and McCaffery⁵⁷ showed relatively large amounts of hysteresis.

Three-Phase Relative Permeabilities

Wettability is a controlling factor in determining three-phase relative permeability characteristics through its effect on the spatial distribution of the three phases.⁵² As discussed in the Introduction, when the wetting is sufficiently strong, the wetting-phase relative permeability is primarily a function of its own saturation and is very similar for both two- and three-phase systems.^{48-50,52,96} This occurs because the wetting phase occupies the small pores and occurs as a thin film on the pore surfaces. The two nonwetting phases, one of which is always the gas, compete for the larger pores. In an oil-wet system, the presence of the trapped gas will affect the water relative permeability because of the interference of these two nonwetting phases. Similarly, in a water-wet system, the trapped gas will usually lower the oil relative permeability by interference and competition for the large flow channels, while the water relative permeability will be relatively unaffected.

Schneider and Owens⁵² examined the effects of a trapped, immobile gas saturation on water/oil relative permeabilities measured in oil-wet Grayburg carbonate and Tensleep sandstone samples. They found almost no effect on the oil (wetting-phase) relative permeability when comparing the two- and three-phase measurements. The water relative permeability was lowered by the trapped gas, showing the interaction between the two nonwetting fluids. Similar results were reported by Emmett *et al.*⁹⁷

Leverett and Lewis⁴⁸ measured three-phase, gas/oil/water relative permeabilities in water-wet sandpacks and found that the relative permeability of the wetting phase (water) was only a function

of water saturation and not dependent on oil or gas saturations. Saraf and Fatt⁹⁸ reported similar results for the water relative permeability during three-phase flow measurements in water-wet Boise sandstone. Schneider and Owens⁵² measured two- and three-phase relative permeabilities on oil-wet Tensleep and water-wet Torpedo sandstone samples and found good agreement between the two- and three-phase relative permeabilities for the wetting phase.

There have been some experiments, however, where the wetting-phase relative permeability depends on the other saturations. Schneider and Owens⁵² studied the effects of trapped gas saturation on a Tensleep plug that was fired at 1,000°F [538°C] to remove all adsorbed compounds and to render it water-wet. They found that the trapped gas saturation affected both the water and oil relative permeabilities. Other experiments have also found that the wetting-phase relative permeability was affected by the nonwetting-phase saturations in water-wet systems.^{28,46,99} It is possible that some of these systems were not strongly water-wet.^{96,98} As an example, Snell⁹⁹ states that polar compounds in the diesel/lubricating-oil mixture that he used may have altered the wettability of his system.

The effect of wettability on the nonwetting-phase relative permeabilities is more complicated because saturation and saturation history are also important. In many cases, the two nonwetting phases will interfere with each other. Schneider and Owens⁵² found that trapped gas in oil-wet Tensleep sandstone and Grayburg carbonate plugs reduced the water relative permeability when compared with two-phase water/oil measurements at the same water saturation. This was expected because the trapped gas and the nonwetting water would be expected to interfere with each other. Schneider and Owens then fired the Tensleep sandstone plug at 1,000°F [538°C] to render it strongly water-wet and measured steady-state water/oil relative permeabilities in the presence of a trapped gas. They found that the nonwetting-phase (oil) relative permeability at high wetting-phase (water) saturations was increased by the presence of trapped gas. This observation remains unexplained.

Conclusions

1. Relative permeabilities are a function of wettability, pore geometry, fluid distribution, saturation, and saturation history. Wettability affects relative permeability by controlling the flow and spatial distribution of fluids in a porous medium.

2. In a uniformly wetted core, the effective oil permeability at a given initial water saturation decreases as the wettability is varied from water-wet to oil-wet. In addition, the water relative permeability increases and the oil relative permeability decreases as the core becomes more oil-wet.

3. In fractionally wetted sandpacks, where the size of the individual water- and oil-wet surfaces are on the order of a single pore, relative permeabilities appear to be similar to those in uniformly wetted systems. The water relative permeability increases and the oil relative permeability decreases as the fraction of oil-wetted surfaces increases.

4. In a mixed-wettability core, the larger, oil-filled pores are oil-wet, while the smaller, water-filled pores are water-wet. The continuous oil-wet paths in the larger pores change the relative permeability curves when compared with a uniformly or fractionally wetted system, and allow the mixed-wettability system to be water-flooded to a very low ROS by the injection of many PV's of water.

5. The most accurate relative permeability measurements are made on native-state core, where the reservoir wettability is preserved. When such core is unavailable, the core should be cleaned and restored. Serious errors can result when measurements are made on core with altered wettability, such as cleaned core or core contaminated with drilling-mud surfactants.

6. The effective water permeability of a cleaned core at the ROS will vary, depending on the effectiveness of the core cleaning method.

7. The wetting-phase drainage and imbibition relative permeabilities show little hysteresis in many strongly wetted systems. However, several unsteady-state experiments have shown little hysteresis in the nonwetting phase, but significant hysteresis in the wetting phase.

8. In many strongly wetted systems, the wetting-phase relative permeability is primarily a function of its own saturation and is very

similar for both two- and three-phase relative permeability measurements.

9. Some researchers recommend that the unsteady-state JBN relative permeability method not be used in strongly water-wet cores because of insufficient time for the fluids to come to wetting equilibrium. Unfortunately, very few data are available either to prove or to disprove this hypothesis.

Nomenclature

- k_a = air permeability, md (Fig. 13)
- k_d = permeability of the displaced phase, md
- k_i = permeability of the injected phase, md
- k_o = oil permeability, md
- k_{owi} = effective oil permeability at initial water saturation, md
- k_{ro} = relative oil permeability
- k_{rw} = relative water permeability
- S_{gr} = residual gas saturation, %PV
- S_{or} = residual oil saturation, %PV
- S_w = water saturation, %PV
- S_{wi} = irreducible water saturation, %PV
- T = temperature, °F [°C]
- θ = contact angle, degrees [rad]
- θ_{adv} = advancing contact angle, degrees [rad]
- ϕ = porosity, %

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SI Metric Conversion Factors

degrees	× 1.745 329	E-02 = rad
ft	× 3.048*	E-01 = m
°F	(°F - 32)/1.8	= °C

*Conversion factor is exact.

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Wettability Literature Survey—Part 6: The Effects of Wettability on Waterflooding

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Summary. The wettability of a core will strongly affect its waterflood behavior and relative permeability because wettability is a major factor controlling the location, flow, and distribution of fluids in a porous medium. When a strongly water-wet system is waterflooded, recovery at water breakthrough is high, with little additional oil production after breakthrough. Conversely, water breakthrough occurs much earlier in strongly oil-wet systems, with most of the oil recovered during a long period of simultaneous oil and water production. Waterfloods are less efficient in oil-wet systems compared with water-wet ones because more water must be injected to recover a given amount of oil.

This paper examines the effects of wettability on waterflooding, including the effects on the breakthrough and residual oil saturations (ROS's) and the changes in waterflood behavior caused by core cleaning. Also covered are waterfloods in heterogeneously wetted systems. Waterfloods in fractionally wetted sandpacks, where the size of the individual water-wet and oil-wet surfaces are on the order of a single pore, behave like waterfloods in uniformly wetted systems. In a mixed-wettability system, the continuous oil-wet paths in the larger pores alter the relative permeability curves and allow the system to be waterflooded to a very low ROS after the injection of many PV's of water.

Introduction

This paper is the sixth in a series of literature surveys covering the effects of wettability on core analysis.¹⁻⁵ Wettability has been shown to affect waterflood behavior, relative permeability, capillary pressure, irreducible water saturation (IWS), ROS, dispersion, simulated tertiary recovery, and electrical properties. Earlier but less complete reviews covering the effects of wettability on waterflooding and relative permeability can be found in Refs. 6 through 17.

Waterflooding is a frequently used secondary recovery method in which water is injected into the reservoir, displacing the oil in front of it. Assuming that the reservoir is initially at IWS, only oil is produced until breakthrough, the time when water first appears at the production well. After breakthrough, increasing amounts of water and decreasing amounts of oil are produced. The process continues until the WOR is so high that the well becomes uneconomical to produce.

Waterfloods in water-wet and oil-wet systems have long been known to behave very differently.¹⁸⁻²² For uniformly wetted systems, it is generally recognized that a waterflood in a water-wet reservoir is more efficient than one in an oil-wet reservoir.^{10,15,18,19,23-28} An example of the effect of wettability on waterflood performance calculations is shown in Fig. 1. Steady-state oil/water relative permeabilities were measured in an outcrop Torpedo sandstone using a mild NaCl brine and a 1.7-cp [1.7-mPa·s] refined mineral oil. The wettability of the system was controlled by adding either (1) various amounts of barium dinonyl naphthalene sulfonate to the oil, which made the system more oil-wet, or (2) Orvus KTM liquid (a detergent) to the brine to achieve a strongly water-wet system with a contact angle of 0° through the brine. Wettability was monitored by contact-angle measurements on a quartz crystal. The measured relative permeability curves were used to calculate field performance, assuming a single 20-acre [8-ha] five-spot with homogeneous properties. Oil and water viscosities were assumed to be 1.74 and 0.35 cp [1.74 and 0.35 mPa·s], respectively. The calculated waterflood results are shown in Fig. 1, where water breakthrough is the point at which each curve first becomes nonlinear. Fig. 1 demonstrates that earlier water breakthrough and less efficient oil recovery occur as the system becomes more oil-wet. For example, 8% less oil will be produced at a WOR of 25 if the contact angle is 138° [2.4 rad], rather than 47° [0.82 rad].

Waterflood recovery is controlled by the oil and water relative permeabilities of a system and by the water/oil viscosity ratio. In

laboratory-scale experiments, inlet and outlet end effects can also affect the recovery. The effects of relative permeabilities and viscosity ratio on waterflooding are demonstrated by the fractional flow equation. If we neglect capillary effects and assume a horizontal system, the simplified form of the fractional flow equation (e.g., see Craig⁶) is

$$f_w(S_w) = \frac{1}{1 + \frac{\mu_w k_{ro}}{\mu_o k_{rw}}}, \dots \dots \dots (1)$$

where

f_w = fractional flow of water,

S_w = water saturation,

μ_o, μ_w = oil and water viscosities, respectively, cp, and

k_{ro}, k_{rw} = oil and water relative permeabilities, respectively.

Eq. 1 shows that the fractional flow of water at a given saturation is increased when the water/oil viscosity ratio is decreased. Decreasing the water/oil viscosity ratio will cause earlier breakthrough and less efficient oil production. Similar effects will occur when the water/oil relative permeability ratio is increased. The oil and water relative permeabilities are explicit functions of the water saturation. They are also affected by pore geometry, wettability, fluid distribution, and saturation history.⁶

Water-Wet Systems. As discussed by Anderson,⁵ wettability has a strong effect on relative permeability. As the core becomes more oil-wet, the water relative permeability increases and the oil relative permeability decreases. The water will flow more easily in comparison with the oil during a waterflood, causing progressively earlier breakthrough and less efficient recovery.^{18,19} Wettability affects relative permeability and waterflood behavior because it is a major factor controlling the location, flow, and spatial distribution of fluids in the core. Craig⁶ and Raza *et al.*¹⁰ have given good summaries of the effects of wettability on the distribution of oil and water in a core. Consider a strongly water-wet rock initially at the IWS. Water, the wetting phase, will occupy the small pores and form a thin film over all the rock surfaces.²⁹⁻³² Oil, the non-wetting phase, will occupy the centers of the larger pores. This fluid distribution occurs because it is most energetically favorable. Any oil placed in the small pores would be displaced into the center of the large pores by spontaneous water imbibition, because this would lower the energy of the system.

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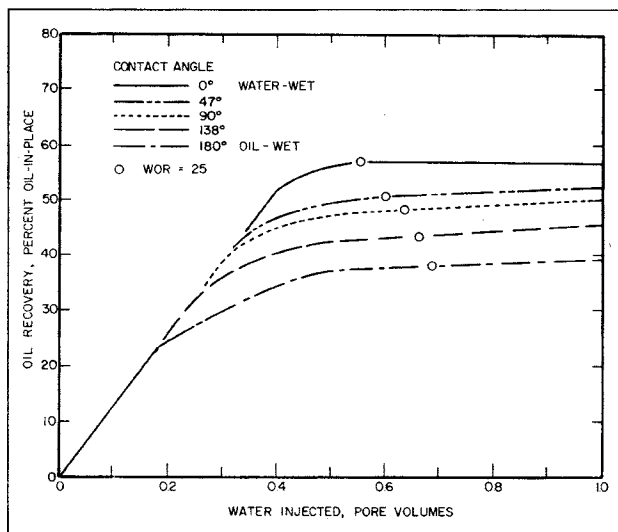


Fig. 1—Effect of wettability on waterflood performance calculations, 20-acre five-spot, $\mu_o = 1.74$ cp, $\mu_w = 0.35$ cp. Taken from Owens and Archer.²⁷

During a waterflood of a water-wet system at moderate oil/water viscosity ratios, water moves through the porous medium in a fairly uniform front.⁶ The injected water will tend to imbibe into any small- or medium-sized pores, moving oil into the large pores where it is easily displaced. Ahead of the front, only oil is moving. In the frontal zone, each fluid moves through its own network of pores, but with some wetting fluid located in each pore.⁶ In this zone, where both oil and water are flowing, a portion of the oil exists in continuous channels with some dead-end branches, while the remainder of the oil is trapped in discontinuous globules. After the water front passes, almost all the remaining oil is immobile. Because of such immobility in this water-wet case, there is little or no production of oil after water breakthrough. The disconnected residual oil exists in two basic forms: (1) small spherical globules in the center of the larger pores and (2) larger patches of oil extending over many pores that are completely surrounded by water.^{6,29-31,33-35}

An idealized example of a waterflood in a strongly water-wet core is given in Fig. 2. A large fraction of the oil in place (OIP) is produced before breakthrough (BT in figures), with very little additional oil recovered after breakthrough. After breakthrough, the WOR increases rapidly. Because little oil is produced after breakthrough, the total oil recovery is essentially independent of the volume of water injected.¹⁰ Note that while the waterfloods in Fig. 2 give a good idea of typical behavior for water-wet and oil-wet sandstone systems, Morrow¹³ has pointed out that the oil recoveries are higher than average laboratory corefloods.

Oil-Wet Systems. In a strongly oil-wet rock, the rock is preferentially in contact with the oil, and the location of the two fluids is reversed from the water-wet case. Oil is generally found in the small pores and as a thin film on the rock surfaces, while water is located in the centers of the larger pores.

The interstitial water saturation appears to be located as discrete droplets in the centers of the pore spaces in some strongly oil-wet reservoirs.¹⁰ A waterflood in a strongly oil-wet rock is much less efficient than one in a water-wet rock. When the waterflood is started, the water will form continuous channels or fingers through the centers of the larger pores, pushing out oil in front of it. Oil is left in the smaller crevices and pores. As water injection continues, water invades the smaller pores to form additional continuous channels, and the WOR of the produced fluids gradually increases. When sufficient water-filled flow channels form to permit nearly unrestricted water flow, oil flow falls to a very low level.⁶

Fig. 2 also contains an example of a waterflood in a strongly oil-wet core. Oil recovery before breakthrough is relatively small, with most of the oil produced after breakthrough. The WOR increases

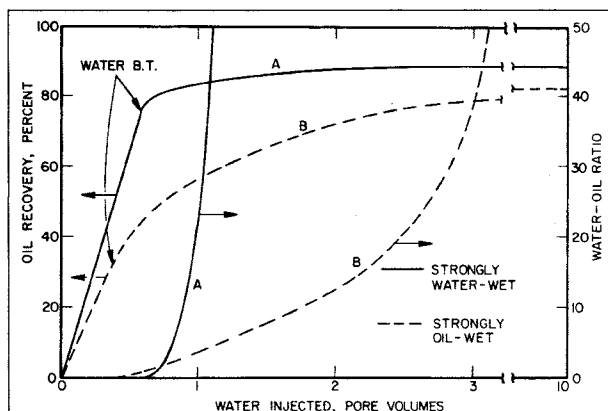


Fig. 2—Typical waterflood performance in water-wet and oil-wet sandstone cores at moderate oil/water viscosity ratios. Taken from Raza et al.¹⁰

gradually after breakthrough. The waterflood in the oil-wet system is less efficient than the waterflood in the water-wet system because more water must be injected to recover a given amount of oil. The residual oil after the waterflood is found filling the smaller pores, as a continuous film over the pore surfaces, and as larger pockets of oil trapped and surrounded by water.²⁹⁻³¹ Because much of this oil is still continuous through the thin oil films and can be produced at a very slow rate,^{29,31,34,35} ROS is not well defined.¹⁰ In contrast to the water-wet case, oil recovery is strongly dependent on the volume of water injected.¹⁰

In the remainder of this paper, the terms "wetting" and "non-wetting" fluid will also be used in addition to water-wet and oil-wet. This will more easily enable us to draw conclusions about a system with the opposite wettability. For example, a waterflood in a system of one wettability will behave in the same manner as an oilflood in the same system with the wettabilities reversed. Relative permeability curves will also show that the fluids can exchange positions and flow behavior.^{36,37}

Breakthrough, Practical, and True Residual Saturations. There are three different oil saturations of interest in waterflooding: breakthrough saturation, practical (or economical) saturation, and true residual saturation. Note that these saturations are all averages over the entire core because the references surveyed report oil recovery as a function of PV's of water injected. All three saturations are essentially equal in a strongly water-wet system with a moderate oil/water viscosity ratio. The saturations can differ greatly, however, in intermediate and oil-wet systems or in water-wet systems with a large oil/water viscosity ratio. Breakthrough occurs when water is first produced at the outlet of the system. Before breakthrough, a volume of oil is produced for each volume of water injected, providing the most efficient recovery possible. The lower the oil saturation in the reservoir rock at breakthrough (and the higher the oil recovery), the more economically attractive a waterflood will be.

After breakthrough, the WOR rises continuously, so that more water must be injected and more water produced for each additional barrel of oil recovered. When the WOR is so high that the waterflood is no longer economical, the system is at the practical or economical ROS. There is general agreement that the practical ROS is lower in water-wet systems; i.e., more oil is produced in a uniformly water-wet system than would be produced in a uniformly oil-wet system with the same pore geometry.^{6,15,26,27,29,38}

When the economical saturation is reached in an intermediate or oil-wet system, there are still continuous connections between much of the oil throughout the porous medium. It is possible to continue to produce small amounts of oil at a very high WOR. Eventually, however, no more oil will be produced, and the true or ultimate residual saturation will be reached. This can take the injection of tens to thousands of PV's of water, depending on the wettability of the system. With mixed-wettability systems, very low true ROS's can be reached, as discussed later.

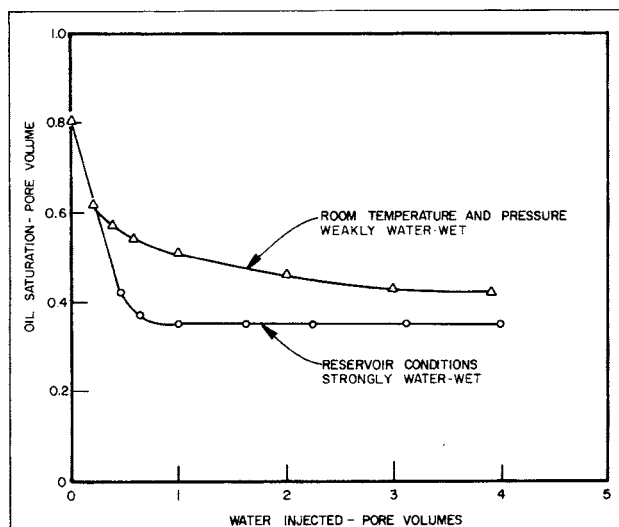


Fig. 3—Effect of wettability on waterflooding, native-state plug. The oil/water viscosity ratio was 1.9. Taken from Kyte et al.²⁴

Note that this literature survey is concerned only with residual saturations that are obtained when capillary forces are predominant. This condition is satisfied when the capillary number (the ratio of viscous to capillary forces) and Bond number (the ratio of buoyancy to capillary forces) are sufficiently low that viscous and buoyancy forces have a negligible effect on residual saturations. Additional oil can be recovered during a waterflood when the viscous or buoyancy forces become important, which will occur when the flow rate is very large or when, for example, a surfactant is used to lower the interfacial tension (IFT). Under these circumstances, wettability effects are also important in the recovery of additional oil, as discussed by Lefebvre du Prey,³⁹ Melrose and Brandner,⁴⁰ Stegemeier,⁴¹ and others.^{7,17,42-45}

Waterfloods in Uniformly Wetted Systems

A typical example of the change in waterflood behavior as a system becomes less water-wet for moderate oil/water viscosity ratios is shown in Fig. 3. A single native-state carbonate plug was waterflooded at two different wettabilities. First, the sample was waterflooded at room temperature and pressure with synthetic formation brine and a refined oil. The viscosity of the refined oil was adjusted to match the reservoir oil/water viscosity ratio. An imbibition test^{2,46} measured with brine and refined oils on additional plugs showed that the native-state core was weakly water-wet at room conditions, because it imbibed a relatively small amount of water (3 to 8% PV). After the room-temperature waterflood, the native-state plug was flushed with live crude oil at reservoir temperature and pressure, then waterflooded at reservoir conditions. Imbibition tests with live crude and brine at reservoir conditions showed that the native-state core was then strongly water-wet, because it imbibed about 50% PV of brine.

The strongly water-wet, reservoir-condition waterflood is much more efficient than the room-condition, weakly water-wet one. The straight line at the left side of the graph shows the recovery before breakthrough, when one volume of oil is produced for each volume of water injected. Breakthrough saturation is the point at which the curve first becomes nonlinear. After water breakthrough, the oil saturation decreases less rapidly because both oil and water are produced at the outlet for each additional volume of water injected. In the strongly water-wet flood (lower curve), breakthrough occurs relatively late and very little oil is produced after water breakthrough. The WOR rises rapidly. In the weakly water-wet flood, however, breakthrough occurs at an earlier time and the WOR rises gradually. More PV's of water must be injected to recover the same amount of oil in the weakly water-wet system. The economical ROS for the weakly water-wet system will be higher (less oil recovered).

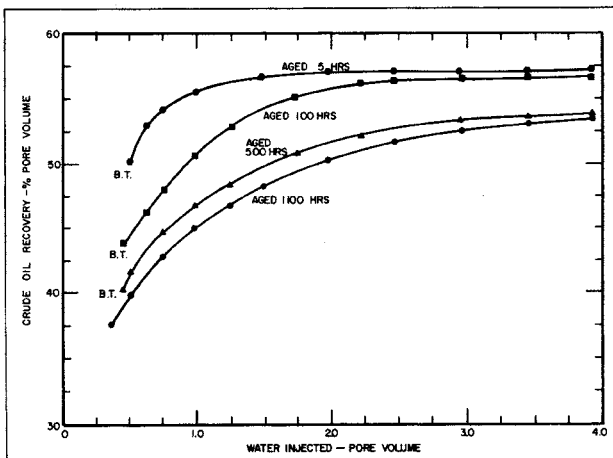


Fig. 4—Effect of aging on waterflood performance of unconsolidated sandpacks, water and live Singleton crude oil. $\mu_o = 1.68$ cp. Taken from Emery et al.⁴⁹

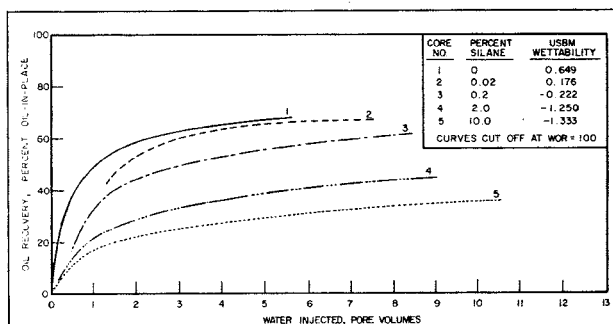


Fig. 5—Effect of wettability on waterflood recovery using brine, Squirrel crude oil, and organochlorosilane-treated Torpedo sandstone plugs. $\mu_o = 33$ cp. Taken from Donaldson and Thomas.²⁹

Similar changes in waterflood and relative permeability behavior in native-state core between reservoir and room conditions have also been observed by others.^{14,47,48} Colpitts and Hunter⁴⁷ compared waterfloods in native-state cores at two different test conditions: (1) reservoir temperature and pressure with brine and live crude and (2) room temperature and pressure with brine and a refined mineral oil. Water breakthrough occurred later in the reservoir-condition tests, and the oil recovery was greater. Colpitts and Hunter also compared waterfloods in native-state core at room conditions with the same core after it had been cleaned. Imbibition tests showed that the native-state core was weakly water-wet, while the cleaned core was neutrally wet. The waterfloods in the cleaned, neutrally wet core were less efficient than the waterfloods in the native-state, weakly water-wet core.

The change in waterflood behavior as wettability is altered is very clearly seen in Fig. 4. Note that this figure is inverted with respect to the preceding one because it shows oil recovered rather than the oil remaining in the core. Although recovery before breakthrough is linear, this is not shown. Initially water-wet sandpacks were saturated with water, driven to IWS with live Singleton crude oil, then aged at 160°F [71°C] and a pressure of 1,000 psi [6.9 MPa], which was sufficient to keep all gas in solution. In Fig. 4, the wettability of the sandpacks during waterflooding ranges from water-wet for the upper curve (aged 5 hours) to oil-wet for the lower curve (aged 1,100 hours). After 1,100 hours of aging, the sandpack had become oil-wet, as determined by an imbibition test. These waterfloods show that as the system becomes more oil-wet, less oil is recovered after breakthrough for the injection of a given amount of water. Donaldson et al.⁵⁰ found similar changes in wettability and waterflood behavior when initially water-wet outcrop cores were aged with brine and crude oil.

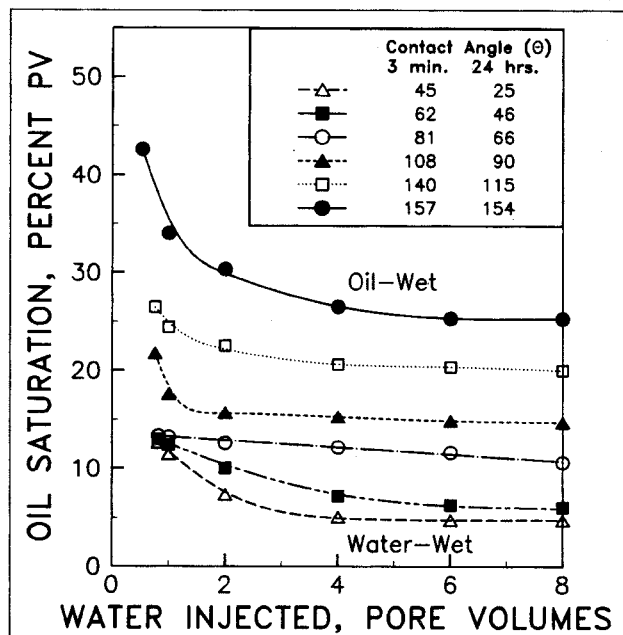


Fig. 6—Effect of wettability on waterflood recovery using brine, a refined mineral oil, and organochlorosilane-treated unconsolidated sandpacks. The system was initially 100% saturated with the refined mineral oil, which had a viscosity of 1.31 cp. Average porosity of the sandpacks was 33.5%, and the average effective oil permeability was 11 darcies. Taken from Newcombe *et al.*⁵⁷

Fig. 5 shows oil recovery for different waterfloods as the wettability was varied from water-wet to oil-wet. The wettability of the core was varied by treatment with organochlorosilanes and measured with the USBM method,^{2,50-52} where +1 indicates a strongly water-wet core, -1 a strongly oil-wet core, and 0 a neutrally wet core. The organochlorosilane-treated cores were saturated with brine, driven with crude to IWS, then waterflooded. Once again, the waterflood is more efficient when the core is water-wet. Other work showing that waterfloods are more effective in water-wet vs. oil-wet cores can be found in Refs. 23, 28, and 53 through 56.

The effects of wettability on oil saturation after breakthrough are shown in Fig. 6. Initially water-wet, unconsolidated sandpacks were treated with different concentrations of organochlorosilanes to vary the wettability. The sandpacks were dried, 100% saturated with a 1.31-cp [1.31-mPa·s] refined mineral oil, then waterflooded with tap water while oil production was monitored. Contact-angle measurements were made with water and oil on a flat silica plate that was treated along with the sandpack. These measurements probably give only a rough indication of wettability for the treated sandpacks. The wettability of a treated core varies with a large number of variables, including the time elapsed since the surface was treated.¹ Newcombe *et al.*⁵⁷ found that the contact angle measured through the water decreased as the system aged. The first column of measurements in Fig. 6 was made after 2 or 3 minutes of aging, while the second column was made after 24 hours of aging.

Fig. 6 shows that the residual saturation after 8 PV of water injection decreases as the system becomes more water-wet, in agreement with the other experiments discussed previously. The oil saturation at breakthrough also decreases as the 24-hour contact angle decreases from 154° to 66° [2.7 to 1.2 rad]. In contrast to the experiments above, however, as the 24-hour contact angle is decreased from 66° to 25° [1.2 to 0.44 rad], the oil saturation at breakthrough remains constant. In addition, the amount of oil production after breakthrough increases, so the strongly water-wet systems are behaving in a somewhat oil-wet manner. Leach *et al.*⁵⁸ pointed out that this behavior was apparently caused by a lack of wetting equilibrium in the water-wet sandpacks. When a water-wet system containing water and oil is in wetting equilibrium, the water will be in contact with the pore walls. The sandpacks used by Newcombe *et al.*, however, were initially 100% oil saturated. During

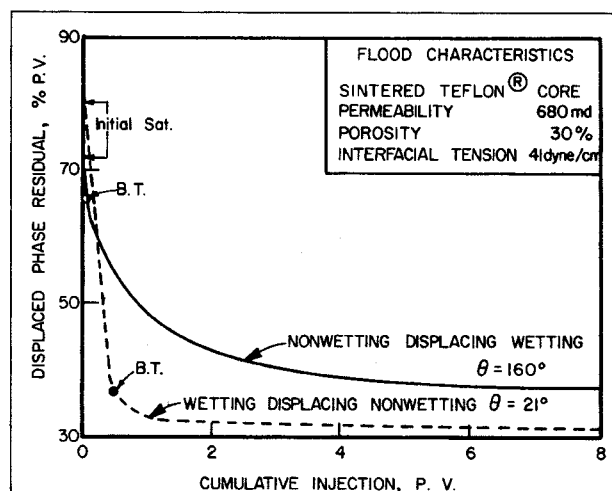


Fig. 7—Effect of wettability on recovery for an unfavorable viscosity ratio of 12. Oil-wet, sintered teflon core, refined mineral oil, and water or a sucrose solution. The contact angle, θ , is measured through the displacing phase on a flat teflon plate. Taken from Mungan.²⁶

a waterflood of this system, the water will eventually displace the oil from the pore walls, but this is a relatively slow process. If water is injected at too high a rate, wetting equilibrium will not be achieved, and the system will appear more oil-wet, with significant oil production after water breakthrough. Leach *et al.* presented results comparing the effects of water injection rate on ROS in water-wet packs with and without an initial water saturation. They found that the apparent oil-wetness of the packs without an initial water saturation increased as the water injection rate increased. In summary, the waterfloods in Fig. 6 show the effects of wettability on waterflooding. However, the floods in the water-wet systems are also affected by the time required for initially 100%-oil-saturated sandpacks to reach wetting equilibrium.

As discussed in the paper on relative permeability,⁵ a number of experimenters have shown that the positions and flow behavior of oil and water are often reversed when relative permeabilities in oil-wet and water-wet systems are compared.^{36,37} Similarly, a waterflood in a system of one wettability will behave in the same manner as an oilflood in the same system with the wettabilities reversed.^{18,19,59} For example, Sarem⁵⁹ treated Burbank cores with DrifilmTM, an organochlorosilane, to render them oil-wet. Cores initially at ROS were oilflooded. Essentially no water production was observed after oil breakthrough for these oil-wet cores, which is analogous to waterflood behavior in a water-wet core.

Mungan^{15,26} compared oilfloods and waterfloods in a sintered teflon core with oil as the wetting fluid. A refined mineral oil and water or a sucrose solution were used. The viscosity ratio was maintained constant by varying the sucrose concentration in the water. Typical results are shown in Fig. 7. For the wetting-displacing-nonwetting case (oilflood), the core was saturated with oil, driven to the ROS with sucrose solution, then oilflooded. A similar procedure was used for the nonwetting-displacing-wetting case (waterflood). The displacement when the wetting fluid is injected (analogous to a waterflood in a water-wet core) is more efficient. Breakthrough occurs later and is followed by only a small amount of two-phase flow.

In summary, when a uniformly water-wet core is waterflooded at a moderate oil/water viscosity ratio, most of the oil is produced before breakthrough and water breakthrough occurs relatively late. The produced WOR rises rapidly after breakthrough.^{10,25} As the system becomes oil-wet, breakthrough occurs earlier. The produced WOR rises more gradually, and a significant amount of oil can be produced after breakthrough.^{10,25} Waterfloods in an oil-wet system are less efficient because more water must be injected to recover a given amount of oil. When a laboratory core is oilflooded, the behavior of the two fluids is reversed. Oilfloods are very efficient when the system is oil-wet and become less efficient when

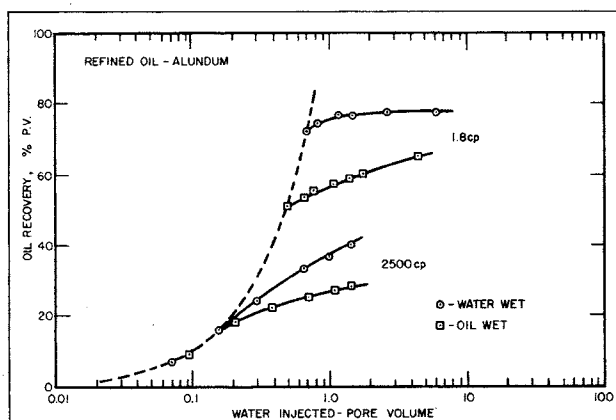


Fig. 8—Effect of wettability and viscosity on waterfloods in oil-wet and water-wet sintered aluminum oxide cores. Taken from Jennings.³⁸

the system is water-wet. Such oilfloods and water/oil relative permeabilities measured with the oil saturation increasing can have practical significance in EOR projects when an oilbank is formed in front of the injected fluids.

Interaction of Wettability and Viscosity Ratio

In the waterfloods at moderate oil/water viscosity ratio discussed previously, wettability was very important in determining waterflood behavior. There was little oil production after breakthrough in a water-wet core, but significant production after breakthrough in an oil-wet core. Actually, the amount of production before and after breakthrough is controlled by both the wettability and the oil/water viscosity ratio, μ_o/μ_w (see Eq. 1). When the oil/water viscosity ratio is large enough, there will be a significant period of two-phase flow at any wettability. An increase in oil viscosity lowers the oil mobility relative to the water mobility. This change in mobility causes an earlier water breakthrough and an increased period of simultaneous oil and water production before ROS is reached.^{6,60}

For example, Richardson⁶¹ examined the effects of viscosity ratio on a 1-ft [0.3-m]-long, water-wet sandpack that was saturated with brine, oilflooded, and then waterflooded ($\mu_w = 1.3$ cp [1.3 mPa·s]). When a 1.8-cp [1.8-mPa·s] oil was used, water breakthrough occurred after about 0.6 PV of water injection with little additional oil recovery. When a 151-cp [151-mPa·s] oil was used, water breakthrough occurred after only 0.3 PV of water injection. After 2.5 PV of water injection, only 0.5 PV of oil had been recovered and additional oil was still being produced. Note that this difference in waterflood behavior was caused only by the change in the oil/water viscosity ratio and not by problems with achieving wetting-phase equilibrium because both waterfloods could be described with the same relative permeability curves.

At high oil/water viscosity ratios, waterfloods in both oil-wet and water-wet cores show a decrease in recovery at breakthrough and a longer period of two-phase production. It is still true, however, that a waterflood in a water-wet core is more efficient than a waterflood in an oil-wet core.^{26,38} At any fixed oil/water viscosity ratio, water breakthrough will occur earlier in the oil-wet core, and more water will have to be injected to obtain the same recovery. An example of the interaction between wettability and viscosity ratio is shown in Fig. 8. The dashed line in Fig. 8 is the oil recovery before breakthrough on this semilog plot. Two refined mineral oils and two artificial cores of sintered aluminum oxide were used. One of the cores was used in its initial water-wet state, while the other was treated with an organochlorosilane to render it oil-wet. The results for the waterfloods with the 1.8-cp [1.8-mPa·s] oil in the oil- and water-wet cores are very similar to those discussed previously. With the 2,500-cp [2,500-mPa·s] oil, breakthrough occurred much earlier, although wettability had little effect on the recovery

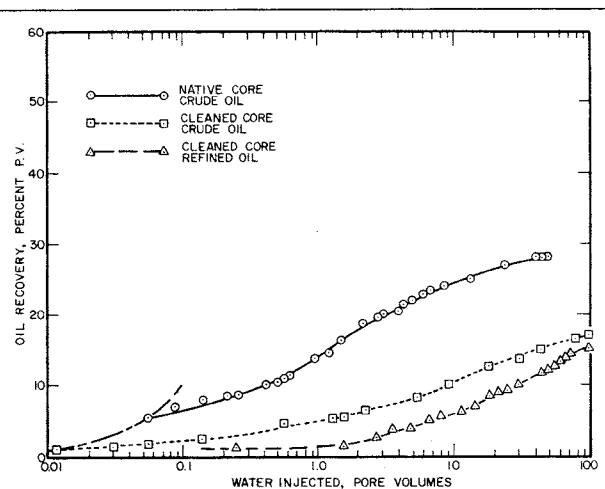


Fig. 9—Waterfloods using 1,200-cp crude or refined mineral oils in native-state or cleaned cores. Taken from Jennings.³⁸

at breakthrough. However, the waterflood in the water-wet core was more efficient after breakthrough.

Jennings³⁸ also compared waterfloods of high-viscosity crudes in native-state and cleaned and friable and unconsolidated cores. Three different waterfloods were compared: (1) live crude in native-state core, (2) live crude in cleaned core, and (3) refined oil in cleaned core. The viscosity of the refined oil was adjusted to match the crude. Typical results are shown in Fig. 9 for waterfloods with 1,200-cp [1,200-mPa·s] oils. The double-dashed line is the oil recovery before breakthrough. The waterflood of the native-state core containing live crude was most efficient, followed by the waterflood of live crude in the cleaned core. Least efficient was the waterflood of the refined oil in the cleaned core. Unfortunately, the wettability before and after extraction was not measured, so it is not known whether the core was more oil-wet or water-wet after cleaning. In addition, the waterflood behavior and wettability of the cleaned core saturated with brine and live crude might depend on the aging time.⁶² Even so, Jennings' results indicate the importance of using native-state cores.

The experiments by Jennings demonstrated that highly unfavorable viscosity ratios cause early water breakthrough for both water- and oil-wet cores. Conversely, when the oil/water viscosity ratio is very favorable, there will be little oil production after breakthrough at any wettability. The waterflood will look similar to waterfloods in strongly water-wet core at moderate oil/water viscosity ratio. Mungan²⁶ examined the effects of viscosity ratio for both the wetting fluid displacing the nonwetting one and the reverse displacement (see Fig. 10). A sintered teflon core, refined mineral oils (wetting phase), and water or a sucrose solution (nonwetting phase) were used. The viscosity ratio was varied by using different sucrose solutions and blends of refined oils. As the viscosity ratio was varied, the contact angle through the wetting phase (oil) varied from about 30 to 50° [0.52 to 0.87 rad], which is reasonably constant.

The upper pair of curves in Fig. 10 show the effects of viscosity ratio when the wetting phase (oil) displaces the nonwetting phase (sucrose solution or water) from a sintered teflon core. The cores were saturated with oil, waterflooded to ROS, and then oilflooded. These displacements are analogous to a waterflood in a water-wet reservoir core. At favorable viscosity ratios, the breakthrough and economic recoveries are essentially equal. As the viscosity ratio becomes more unfavorable (analogous to a higher oil viscosity in a water-wet reservoir core), both the breakthrough and economic recoveries decrease. The breakthrough recovery is slightly smaller than the economic one. These results agree with the recoveries obtained when flooding a water-wet core at moderate oil/water viscosity ratios.

The lower pair of curves in Fig. 10 show the viscosity ratio vs. the recovery when the nonwetting phase (sucrose solution or water) displaces the wetting phase (oil) from the teflon core. The cores

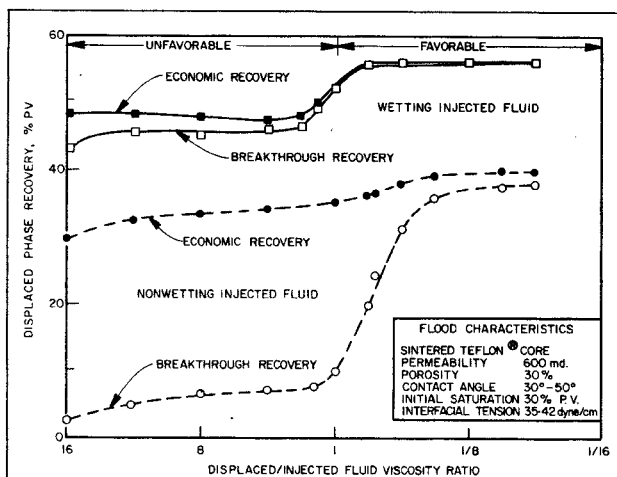


Fig. 10—Effect of viscosity ratio on recovery, sintered teflon core, refined mineral oil, and sucrose solution or water. The upper pair of curves are the recovery when a wetting fluid (refined mineral oil) displaces a nonwetting fluid (sucrose solution or water), which is analogous to a waterflood in a water-wet core. The lower pair of curves are the recovery when a nonwetting fluid displaces a wetting fluid, analogous to a waterflood in an oil-wet core. Taken from Mungan.²⁸

were saturated with water, oilflooded to IWS, and then waterflooded. These displacements are analogous to a waterflood in an oil-wet reservoir core. When the viscosity ratio is unfavorable, most of the nonwetting phase is recovered after breakthrough, in agreement with results discussed above for waterfloods in oil-wet cores. As the viscosity ratio becomes more favorable, the breakthrough recovery gradually approaches the economic recovery. A comparison of the two sets of curves shows that the breakthrough and economic recoveries are lower when the nonwetting fluid is injected. In addition, Fig. 10 demonstrates that there will be very little two-phase production until the economic recovery is reached at a very favorable viscosity ratio, regardless of the wettability.

In unsteady-state relative permeability measurements, a core initially at IWS is waterflooded. Relative permeabilities are calculated from the pressure drop and the produced fluids by the Johnson-Bossler-Naumann method.^{60,63,64} Because a significant amount of oil production is required after breakthrough to calculate relative permeabilities, viscous oils are generally used to increase the period of simultaneous oil and water production. Because viscous oils are used, the shape of the waterflood curve may not be an indication of the wettability and should be interpreted with caution. Core is water-wet if there is little production after breakthrough. On the other hand, two-phase production after breakthrough may be caused by either viscosity or wettability effects.

Residual Saturations in Uniformly Wetted Systems

In this section, the effects of wettability on the breakthrough, practical, and ultimate ROS's in uniformly wetted systems will be discussed. Unfortunately, the conclusions must be considered to be tentative. Experimental results, particularly in strongly water-wet systems, often disagree. In addition, a large number of other variables affect the oil saturation during waterflooding, including viscosity ratio, saturation history, pore geometry, and injection rate. Inlet and outlet end effects can also affect the measured oil saturation in laboratory-scale experiments. Finally, the experiments discussed below report the average saturation in the core, which will be affected by core length. During a waterflood, the oil saturation is higher at the outlet end of the core and decreases toward the inlet because of the unsteady nature of the flood. The average saturation measured at any given time will depend on the saturation throughout the core and vary for cores of different lengths.

Despite the large number of other variables affecting the oil saturation, some generalizations about wettability effects can be made.

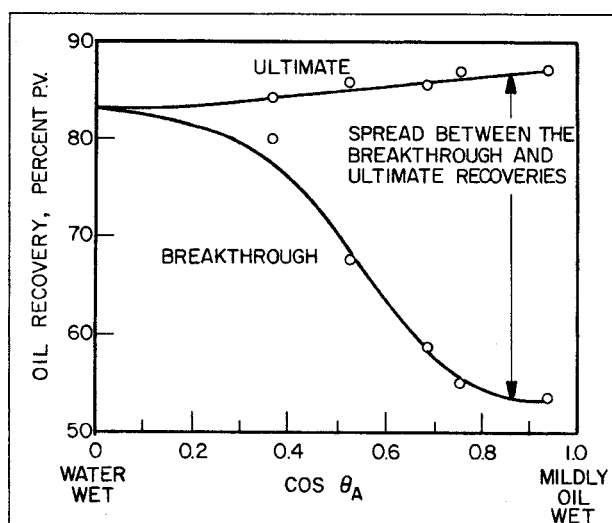


Fig. 11—Effect of wettability on oil recovery, organochlorosilane-treated Pyrex glass core. The two fluids used were brine ($\mu_w = 0.94$ cp) and a mixture of n-dodecane and mineral oil ($\mu_o = 1.98$ cp). Taken from Warren and Calhoun.⁸³ (The labels "water-wet" and "mildly oil-wet" are based on our interpretation of the data.)

There is general agreement in the literature with the following statements for uniformly wetted systems, although exceptions are known to exist.

1. The breakthrough, practical (economical), and ultimate ROS's are essentially equal and low for water-wet systems. After breakthrough, there is almost no oil production. The oil recovery is high in this case because oil recovery is inversely related to the ROS.^{10,18,19,24,26,29,49,53}

2. As the system becomes more oil-wet, the breakthrough and economical ROS's increase, so oil recovery decreases. The economical ROS is lower than the breakthrough saturation, and the difference between the two gradually increases. Small amounts of oil are produced for a long time after breakthrough, so the economical ROS depends on the number of PV's of water injected.^{10,18,19,24,26,28,29,49,53,56,57}

3. The ultimate ROS, which is the saturation after a large number of PV's of water are injected, is only weakly dependent on the wettability. It is slightly lower near neutral wettability (higher oil recovery), but changes much less than the breakthrough or economical oil saturations.^{17,25,53,65}

4. There is some disagreement on the effect of wettability as a core becomes very strongly water-wet compared with moderately water-wet systems. All three ROS's are essentially the same, because there is little production after water breakthrough, with all the oil trapped in discontinuous globules. Different experiments suggest, however, that the ROS in a strongly water-wet system decreases,^{24,29} remains the same,⁶⁶ or increases,^{31,48,66} depending on such variables as heterogeneity, pore geometry, injection rate, and inlet and outlet end effects.

Note that we are discussing the effects at low-to-moderate oil/water viscosity ratios on the order of 1 to 10. As discussed previously, the breakthrough and economical ROS's increases as the oil viscosity increases; however, waterfloods are still more efficient in water-wet systems than in oil-wet ones (see Eq. 1).

Breakthrough Saturations

Figs. 2 through 7 show the changes in breakthrough saturation as the wettability ranges from water-wet to oil-wet. As the core becomes more oil-wet, the oil saturation at breakthrough increases and the oil recovery decreases. In a water-wet core, oil is trapped behind the water front in discontinuous globules. After the water front passes, almost all the remaining oil is immobile, allowing little or no production after breakthrough.^{6,10,29-31,33,35} As the system becomes more oil-wet, the water begins to travel preferentially in

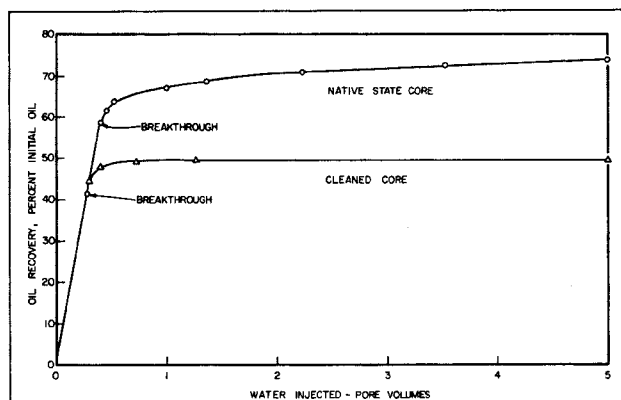


Fig. 12—Comparison of a waterflood in a native-state core vs. a waterflood in the same core after it was cleaned and rendered strongly water-wet. Taken from Rathmell *et al.*⁴⁸

the largest pores, with only weak imbibition into smaller ones. This causes early breakthrough because many pores are bypassed. Because the oil in the core remains connected, however, additional oil can be produced after breakthrough.^{6,10,29-31,35}

For example, breakthrough in the more water-wet case of Fig. 3 occurs when the oil saturation is roughly 0.4, with very little oil recovered thereafter. The upper, weakly water-wet curve gives an earlier breakthrough when the oil saturation is about 0.6 and a much longer period of two-phase flow. In Fig. 4, the breakthrough (BT in the figure) oil recovery was 50% PV when the sandpack was water-wet (aged 5 hours). Breakthrough recovery decreased to about 37% when the sandpack was oil-wet (aged 1,100 hours). The effect of wettability on the breakthrough saturation is also shown in Fig. 11, which will be discussed in more detail later.

As the oil/water viscosity ratio increases, the oil recovery at breakthrough decreases for both water-wet and oil-wet systems (see Figs. 8 through 10). With the high-viscosity oils used by Jennings,³⁸ breakthrough occurred very early for all of the systems. In the system shown in Fig. 8, wettability effects on breakthrough were unimportant for the 2,500-cp [2,500-mPa·s] oil. Alternatively, Fig. 9 clearly shows that wettability can still affect breakthrough even with very-high-viscosity oils.

When a core becomes very strongly water-wet, oil recovery can increase, decrease, or remain the same, depending on other variables such as heterogeneity, pore geometry, and injection rate. In addition, inlet and outlet effects can affect the recovery in laboratory-scale experiments. Although the experiments discussed previously found an increase in recovery, other experimenters have found the recovery to decrease or remain the same when compared with the recovery in moderately water-wet core. The upper curve in Fig. 12 is the oil recovery for a native-state core. Breakthrough occurs relatively late, and there is some oil production after breakthrough. The lower curve, with an earlier breakthrough and little subsequent recovery, is for the same core after it was cleaned and rendered strongly water-wet. An imbibition wettability test^{2,24,46} determined that the cleaned core was strongly water-wet, because it rapidly imbibed a large volume of water. The native-state core was more weakly water-wet, according to imbibition measurements, so breakthrough and practical recovery decreased as the core became more water-wet. Note that it is not known whether the native-state core had nonuniform wettability. As discussed in more detail later, mixed-wettability cores can also show more recovery than strongly water-wet ones.

Amott⁶⁶ examined waterflood recovery in Ohio sandstone and AlundumTM plugs treated with various concentrations of organochlorosilanes to vary wettability. The fluids were brine and kerosene, while wettability was measured by the Amott method.⁶⁶ Fig. 13 shows the recovery after 2.4 PV of water was injected. Amott found that the breakthrough recovery curves had a similar shape. The lower curve in Fig. 13, for the Ohio sandstone plugs, has a maximum as the Amott wettability index varies from water-wet to oil-wet. The recovery at 2.4 PV's increases as the wettability var-

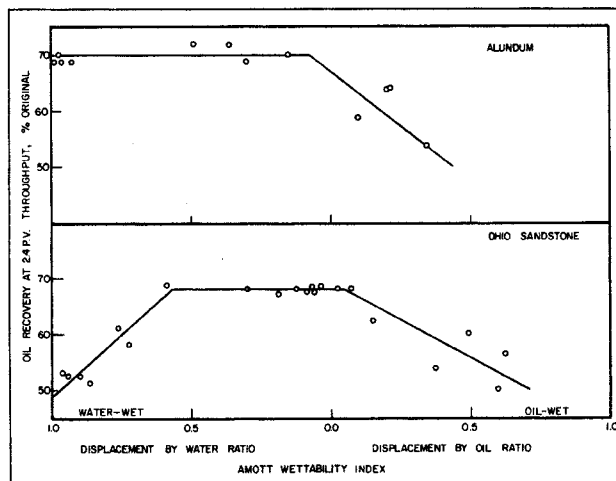


Fig. 13—Amott wettability index vs. waterflood oil recovery after 2.4 PV water injection. Brine and kerosene, organochlorosilane-treated Ohio sandstone and Alundum plugs. Taken from Amott.⁶⁶

ies from strongly water-wet (displacement-by-water ratio = +1) to water-wet (displacement-by-water ratio = 0.5). The recovery remains constant as the wettability varies from water-wet to neutrally wet (both displacement ratios = 0). It is constant, then decreases as the wettability varies from neutral to oil-wet (displacement-by-oil ratio = +0.5). Because the Amott wettability test is not very sensitive near intermediate wettability, the width of the maximum is large.²

Similar data for breakthrough were observed by Rathmell *et al.*⁴⁸ as the wettability was varied in 7- to 9-ft [2.1- to 2.7-m] - long Berea cores treated with various concentrations of Drifilm to vary wettability. Imbibition tests were used to measure the wettability. Breakthrough occurred at an oil saturation of 40% PV for untreated, strongly water-wet cores and at roughly 33% PV for moderately water-wet ones treated with a 0.3% Drifilm solution. Cores treated with higher concentrations of Drifilm were very weakly water-wet, with only very small amounts of water imbibition. The oil saturation at breakthrough for these cores decreased further, to roughly 24% PV.

The upper curve in Fig. 13, which is for an Alundum core (sintered aluminum oxide), has a constant recovery until intermediate wettability is reached, followed by a decline in recovery with increasing oil-wetness. The difference in the two curves shows that the wettability and pore geometry interact to influence the recovery. In the Alundum core, which is relatively homogeneous, wettability effects are less important. Similarly, Morrow⁶⁷ found that the residual saturation reached during a capillary pressure measurement is not influenced by wettability when the porous medium (a bead pack) is sufficiently homogeneous.

Microscopic nonuniformities and heterogeneities can lower oil recovery by making it easier for oil to be bypassed and trapped,⁶⁶ particularly in strongly water-wet or oil-wet systems, where the capillary forces causing fluid isolation and trapping are strongest. Moore and Slobod³¹ noted that water will tend to imbibe into the smallest pores when waterflooding a strongly water-wet rock. In a strongly water-wet system, tracer studies show that a relatively large fraction of the nonwetting fluid (oil) is located in nonflowing dendritic structures, particularly at saturations near ROS.⁶⁸ As the injected water bypasses them, the dendrites are trapped and isolated by capillary forces. Heterogeneities increase the ROS by making it easier for the water to bypass and trap the oil.

Wardlaw⁶⁹ used glass micromodels to observe the increased trapping caused by heterogeneities in strongly water-wet systems. The micromodels contained either large single pores or isolated clusters of large pores surrounded by a continuous network of smaller pores. Experiments were made with both air/mercury, where air was the wetting fluid, and water/air, where water was the wetting fluid. In each case, the wetting fluid displaced the nonwetting fluid from the model (analogous to a waterflood in a water-

wet core). The wetting fluid advanced more rapidly in the fine pores compared with the large pore, bypassing the nonwetting fluid in the large pores and isolating it. Wardlaw then made one of his systems neutrally wet by coating it with a plastic and repeated the water-displacing-air experiments. He found much less trapping of the air in the large pores, indicating that heterogeneities were less important in his neutrally wet system.

Heterogeneities are also important in determining the residual wetting phase in strongly wetted systems (i.e., oil in an oil-wet system). When the nonwetting phase is injected, it will tend to travel through the larger pores, bypassing wetting fluid located in clusters of smaller pores. Morrow⁷⁰ used capillary pressure measurements to compare the IWS in strongly water-wet, homogeneous and heterogeneous sandpacks. The sandpacks were composed of different fractions of large and small grains. In the homogeneous sandpacks, the large and small grains were mixed together, so the pore size was relatively uniform throughout the pack. In this case, the ROS was roughly 8% PV, regardless of the fraction of small vs. large grains.

The heterogeneous packs were composed of clusters of small grains (small pore size) in a continuous matrix of large grains (large pore size). In this case, the IWS was much higher, from 20 to 40% PV, depending on the fraction of smaller grains. The IWS was increased because water was trapped in the clusters of small pores. During the capillary pressure measurements, the water would drain from the large pores, disconnecting and trapping the water in the small pores. The work by Wardlaw and Morrow indicates the interaction of heterogeneities and wettability in determining residual saturations.

Changes in Saturation Caused by Inlet and Outlet End Effects

Inlet and outlet end effects are not important on a reservoir scale. However, they can significantly affect measured oil saturations and recoveries in laboratory-scale experiments. The outlet end effect is the accumulation of the wetting phase at the outlet caused by local capillary forces.⁷¹⁻⁷⁴ In a water-wet core, capillary forces cause a high water saturation near the outlet, retarding water breakthrough.⁷³ During the waterflood of a water-wet core, the capillary pressure, $P_c = p_o - p_w$, is positive in the interior of the core, so the water pressure is less than the oil pressure. In contrast, the capillary pressure outside the core is zero because the interfaces between the oil and water are almost flat. When the water first arrives at the outlet of the core, the pressure in the water is lower than the pressure in the oil surrounding the outlet face; hence no water will be produced.^{73,74} Because water cannot be produced, it accumulates near the outlet, allowing the capillary pressure to decrease. When enough water has accumulated, the ROS is reached in a thin layer near the exit, where the capillary pressure is zero. At this point, water breakthrough occurs because the capillary pressures inside and outside the core are equal. The outlet end effect is largest at low flow rates, where capillary forces also cause a spreading of the displacement front. These two effects cause a delay in water breakthrough compared with the time that water first arrives at the end face of the core. To avoid this problem, most waterflooding experiments are designed to minimize the outlet end effect and the influence of capillary pressure on the displacement front by increasing the flooding rate or the core length.⁷³⁻⁷⁵ When the flooding rate is increased, the zone of excess water accumulation shrinks until it is negligible, causing the arrival and breakthrough of water to occur simultaneously.

For strongly water-wet cores, there is evidence that increasing the flow rate to minimize the outlet end effect increases the severity of an inlet end effect. An inlet end effect develops in strongly water-wet media as the result of spontaneous, localized counterflow imbibition.^{57,73,76,77} Injected water will first contact the inlet face of the core in a localized area. If the wetting is strong enough, water will spontaneously imbibe into the core at the point of contact, causing a simultaneous counterflow of oil out of the core. Water continues to enter in this localized region as the flood continues, establishing a region of unstabilized, nonlinear flow.⁷³ As the flood proceeds, capillary forces redistribute the water over the entire cross-sectional area of the core. The inlet end effect will be

most important in short cores and at high injection rates, where the influence of capillary forces is relatively small. Where capillary forces have sufficient time to redistribute the water, the inlet effect will be negligible; e.g., in a reservoir. Kyte and Rapoport⁷³ ran waterflooding experiments with water and glycerine solutions, and a refined oil in artificial, strongly water-wet, sintered aluminum oxide cores. They showed that the inlet end effect was important when the injection rate was high enough that the outlet end effect was negligible. The inlet end effect caused a decrease in the oil recovery at water breakthrough. However, the inlet end effect did not significantly affect the overall flooding behavior. The oil recovery curve after breakthrough converged rapidly to the curve from a longer core where both inlet and outlet end effects were negligible.

During a waterflood of an oil-wet core, capillary forces will keep the oil saturation near the core outlet high, even after the remainder of the core is at ROS.^{72,75,78} At low flow rates, the end effect and the spreading of the displacement front caused by capillary forces will reduce the oil recovery at breakthrough.⁷⁸ As with water-wet cores, oil-wet cores are generally flooded at rates high enough that the outlet end effect and the effects of capillary forces on the displacement front are both negligible. Rapoport and Leas⁷⁸ found that the effects of capillary forces were minimized when

$$L\mu_w u \geq 1 \text{ through } 5, \dots \dots \dots (2)$$

where L is the core length, cm, and u is the flow rate per unit cross-sectional area, cm/min.

Hinkley and Davis⁷⁹ studied end effects in composite cores, which consist of a series of short core plugs butted together. Saturations along the length of the core were measured with a microwave scanner. Water-wet Berea sandstone, water-wet Baker limestone, and oil-wet TegrilasTM plugs were used. Tegrilas is a synthetic porous medium composed of uniformly sized beads epoxied together. Hinkley and Davis found that even when the plugs were carefully machined and placed under compression, saturation discontinuities could occur between the plugs, giving rise to end effects in each plug in the series. These end effects could be reduced by adding a "bridging" material between the plugs, with comparable wettability and permeability. For water-wet plugs, they found that two water-wet bridging materials, tissue paper and filter paper, were both effective. Water-wet diatomaceous earth was also effective, but there was some indication of deterioration with time. A water-wet glass fiber membrane and an oil-wet teflon filter membrane were both found to be ineffective. For the oil-wet Tegrilas plugs, Hinkley and Davis were not able to find an effective bridging material. They tried both water-wet tissue paper and oil-wet teflon filter membranes.

Hinkley and Davis found that the end effects between the plugs could also be minimized by increasing the injection rate for both oil-wet and water-wet plugs. To estimate the flow rates that should be used during floods of composite cores, they recommend the Rapoport and Leas scaling criteria (Eq. 2) with the total length replaced by the length of the individual plugs.

Practical ROS

The economical (practical) oil recovery varies in a fashion similar to breakthrough recovery, although it decreases more slowly as the system becomes more oil-wet. The breakthrough and economical recoveries are essentially identical in a water-wet core with a moderate oil/water viscosity ratio because little additional oil is recovered after breakthrough. As the system becomes more oil-wet, much more oil is produced in two-phase flow after breakthrough, and the economical recovery becomes larger than the breakthrough recovery. Because oil recovery and ROS are inversely related, the practical ROS increases at a slower rate than the breakthrough saturation.

The effects of wettability on breakthrough and practical oil saturations (recoveries) are shown in Figs. 2 through 7. Recall that the breakthrough saturation (recovery) occurs when the slope of the curve first changes. When the economical ROS is reached, very little additional oil is produced for each additional PV of water injected, making the produced oil curve almost horizontal.

In the lower, more water-wet curve of Fig. 3, the breakthrough and economical ROS's are about 41 and 36% PV, respectively, a difference of only 5% PV. In the upper, weakly water-wet curve, the breakthrough saturation is about 62 percent PV, while the economical ROS is about 42% PV, a difference of about 20% PV. A comparison of the two curves shows that as the system became less water-wet, the economical ROS increased by a relatively small amount, 6% PV, while the breakthrough saturation increased by a much larger amount, 20% PV.

This slower change in the economical residual saturation compared with the breakthrough saturation can also be seen in Fig. 7, where a flood with the nonwetting fluid displacing the wetting fluid (similar to a waterflood in an oil-wet core) is compared with the reverse displacement (wetting fluid displacing the nonwetting fluid, similar to a waterflood in a water-wet core). When the differences in the initial saturations are taken into account, the economical recoveries are very similar, while the recoveries at breakthrough differ by about 20% PV. Similarly, Figs. 2, 4, and 5 show the economical recovery decreasing more slowly than the breakthrough recovery as the oil-wetness increases (economical ROS increasing more slowly).

As the oil/water viscosity ratio (μ_o/μ_w) increases, the economical oil recovery decreases for both water-wet and oil-wet systems (see Figs. 8 through 10). However, it is still generally true that it is more efficient to waterflood a water-wet system than an oil-wet one.

True Residual Saturation

On the basis of a limited number of experiments, it appears that the ultimate oil recovery, which occurs after the injection of many PV's of water, has a maximum under neutral or slightly oil-wet conditions.^{17,25,56,65} The ultimate recovery corresponds to the minimum true residual saturation and declines as the system becomes more strongly wetted in either direction. The change in recovery as the wettability is altered is relatively small, however, and the ultimate recovery is much less dependent on the wettability than either the breakthrough or economic recoveries.

The true ROS does not appear to be affected by the oil/water viscosity ratio. Rathmell *et al.*⁴⁸ found no significant effect on the ROS in water-wet and intermediate-wet core when the oil/water viscosity ratio ranged from 1 to 50. While the viscosity ratio does not affect the final recovery, note that some oil-wet systems require a very large number of PV's of water before ultimate oil recovery is reached, particularly at high oil/water viscosity ratios. Similarly, Slobod⁸⁰ found that a large number of PV's of naphtha (0.44 cp [0.44 mPa·s]) were required to flood brine-filled (1 cp [1 mPa·s]), water-wet cores to IWS. This displacement with an unfavorable viscosity ratio is analogous to a waterflood in an oil-wet core. In one case, the water saturation at oil breakthrough was roughly 40% PV. Small amounts of water were produced for a very long time after breakthrough. Roughly 1,200 PV's of naphtha was required to achieve the IWS of 15% PV.

Jennings⁵³ compared the oil saturations during waterfloods in water-wet and organochlorosilane-treated, oil-wet sintered aluminum oxide plugs. The plugs were initially 100% saturated with kerosene, then waterflooded. The water saturations at breakthrough were very different: roughly 75 and 53% PV for the water- and oil-wet plugs, respectively. After 40 PV of water injection, however, the water saturations were roughly 85% PV for the water-wet plug, and 81% PV for the oil-wet one. The oil recovery for the oil-wet plug was still slowly increasing, while it had ceased for the water-wet plug, demonstrating that the ultimate ROS's would be very similar for the oil-wet and water-wet plugs if flooding had continued.

Fig. 14 shows the ultimate oil recovery after waterflooding as a function of the wettability. The sessile-drop ratio, a method of contact-angle measurement, was used to measure the wettability.^{81,82} In this method, a drop of oil is placed on the underside of a smooth silica surface immersed in brine. The ratio, the height divided by the diameter of the drop, is measured after the system reaches equilibrium. The drop is small enough that gravitational effects are negligible and may be considered to be a segment of a sphere, making it possible to calculate the contact angle. A sessile-drop ratio of 0 corresponds to an oil-wet core ($\theta=180^\circ$ [3.14 rad]),

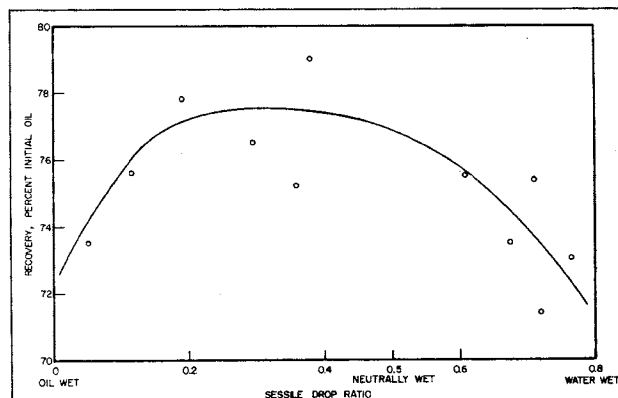


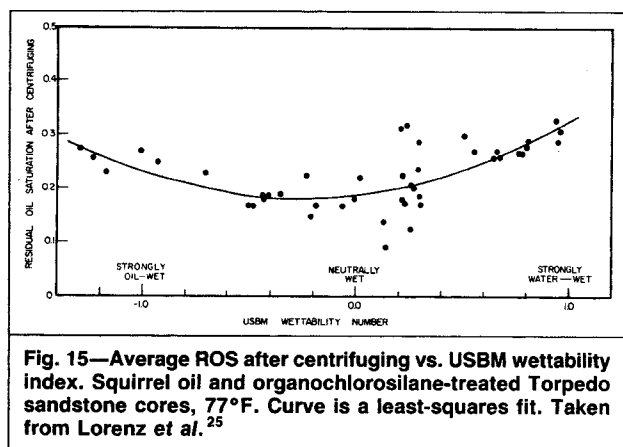
Fig. 14—Effect of wettability on ultimate oil recovery, synthetic silica core, East Texas crude oil, and surfactant-treated brine. Taken from Kennedy *et al.*⁶⁵

a ratio of 0.5 to an intermediate-wet core ($\theta=90^\circ$ [1.57 rad]), and a ratio of 1 to a water-wet core ($\theta=0^\circ$). The waterflooding experiments used an artificial core of chemically consolidated sand, brine, and East Texas crude oil. Different surfactants in the fluids were used to vary the wettability, while maintaining a constant IFT. The maximum recovery (and minimum true residual saturation) occurred at a slightly oil-wet condition. As the wettability varied, however, the change in true ROS was small, about 5%. Kennedy *et al.*⁶⁵ also looked at ROS in outcrop Woodbine sandstone cores but found that the data were too scattered to draw conclusions. At least part of the scatter occurred because the IFT was not controlled in this second set of experiments.

Warren and Calhoun⁸³ measured breakthrough and ultimate recoveries on sintered PyrexTM glass cores, varying the wettability with different concentrations of Drifilm. Brine and mixtures of organic liquids were used. The ultimate recovery was defined as the oil recovered after 20 PV of brine injection. In their experiments, the cores were first completely saturated with the organic liquid (oil), then the breakthrough and ultimate recoveries were measured during a constant-rate waterflood. Typical results are shown in Fig. 11. Warren and Calhoun measured an apparent contact angle, θ_a , and assumed that the wettability of their experiments varied from neutrally wet ($\cos \theta_a=0$) to strongly oil-wet ($\cos \theta_a=1$). Because of this, their work is often cited as the only experiment in the literature where the maximum waterflood recovery occurred under strongly oil-wet conditions ($\theta=180^\circ$ [3.14 rad]). As discussed in detail in the Appendix, however, we feel that the best interpretation of these experiments is that the wettability actually varied from mildly water-wet to mildly oil-wet. With this interpretation, the breakthrough recovery is high when the system is water-wet, dropping sharply as the system becomes mildly oil-wet. The ultimate recovery rises slightly, with the largest value under mildly oil-wet conditions. With this interpretation, the data from Warren and Calhoun's experiments agree with the other literature cited.

The trapping of oil and gas on a microscopic scale is affected by the geometric and topologic properties of the pores, the fluid properties, and the wettability.⁶⁹ It is generally accepted that maximum recovery will occur near neutral wettability because the IFT's that disconnect and trap the oil are minimized.^{17,48,69,84,85} In a strongly water-wet system, the water will tend to travel through the smaller pores, possibly bypassing some of the oil in the larger pores.³¹ In addition, the strong interfacial forces will tend to disconnect and to "snap off" some of the oil. In a strongly oil-wet system, there is a tendency for the water to finger through the larger pores, also bypassing some of the oil.³¹ In contrast, there will be less tendency for the water to bypass and trap oil at neutral wettability.

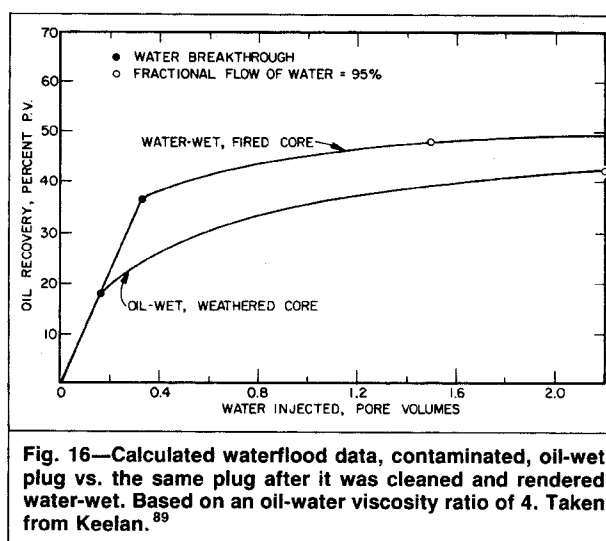
Experiments by Wardlaw^{69,85} in glass micromodels support the hypothesis that trapping on a microscopic scale is minimized near neutral wettability. As discussed earlier, Wardlaw⁶⁹ found less trapping in heterogeneous glass micromodels at neutral wettability than in the micromodel when it was strongly water-wet because



there was less tendency to bypass and to trap the displaced phase. In a second set of experiments, Wardlaw⁸⁵ examined one mechanism of trapping, isolation of the displaced phase in a single pore by a capillary instability (snap-off) between the pore and an adjacent pore throat. A strongly water-wet glass micromodel consisting of a series of pore/pore-throat pairs was saturated with brine, then displaced with air to IWS. Water was then allowed to imbibe into the system. In this strongly water-wet case, the water traveled around the outside of the pore, bypassing most of the nonwetting phase (air) in the center of the pore. When the water reached the exit throat, a capillary instability trapped and isolated the remaining nonwetting phase by snapping off its connection in the pore throat. Wardlaw then treated the glass surface with a water-repellent silicone, which caused a water/oil contact angle of about 90° [1.57 rad] (neutral wettability). When the experiment was repeated, the water interface advanced smoothly through the tube, not allowing any of the displaced air to be trapped. Wardlaw repeated his experiments with different fluid pairs and surface treatments to vary wettability. He found significant trapping when the contact angle was less than about 20° [0.35 rad]. Above 20° [0.35 rad], the trapping decreased significantly. For contact angles greater than about 35° [0.61 rad], no residual air was trapped. Wardlaw's experiments examined only a few of the large number of different mechanisms that can trap oil. They demonstrate, however, that these mechanisms become much less effective near neutral wettability.

In summary, breakthrough, economical, and true residual saturations are essentially equal for water-wet cores at low-to-moderate oil/water viscosity ratios, on the order of 1 to 10. For these conditions, residual oil is left as discontinuous globules. Maximum breakthrough and practical (economical) oil recoveries are reached under water-wet conditions, while the maximum ultimate recovery occurs when the system is neutrally to mildly oil-wet. Maximum recovery decreases in a strongly oil-wet core because the water travels preferentially through the largest pores, bypassing much of the oil. When the core becomes very strongly water-wet, oil recovery may increase, decrease, or remain the same, depending on the pore geometry, heterogeneity, and inlet and outlet end effects.

Comparison With Capillary Pressure Data. In the experiments discussed previously, capillary forces dominate the processes that trap residual oil in a core. In contrast, neither buoyancy nor viscous forces are important in trapping. These forces may also be neglected in capillary pressure measurements. Because the forces determining ROS are the same, one would expect the residual saturation determined from the capillary pressure curve to be similar to the ultimate ROS after waterflooding. Fig. 15 shows the variation in ROS with wettability measured in an outcrop sandstone with brine and crude oil. Note that the ROS data presented by Lorenz *et al.*²⁵ refer to the average saturation of the core, not the face saturation determined by Hassler and Brunner's⁸⁶ and Slobod *et al.*'s⁸⁷ methods. The average saturation is always somewhat higher than the face saturation, approaching it as the capillary pressure difference across the core is increased. In presenting these data, an assumption has been made that the capillary pressure is high enough for the average and face saturations to be essentially equal.



In these tests, the wettability was varied by use of different concentrations of Drifilm and assessed with the USBM wettability index, *W*. ROS decreases from roughly 30% when the core is strongly oil- or water-wet to about 20% when the system is neutrally wet. The curve reaches a minimum at a slightly oil-wet condition, when *W* is slightly less than zero. This is in good agreement with the waterflood measurements by Kennedy *et al.*,⁶⁵ keeping in mind that the figures are inverted with respect to each other.

Effect of Trapped Gas on Waterflood Recovery

Some evidence suggests that gas has different effects on ROS's in water-wet and oil-wet porous media. As reviewed in Craig,⁶ the ROS in water-wet systems is lower when cores contain a trapped gas saturation during a waterflood compared with waterfloods with no trapped gas. This result was confirmed in experiments by Kyte *et al.*⁸⁸ in water-wet systems. However, several experiments by Kyte *et al.* indicate no effect of gas saturation on the ultimate ROS in oil-wet systems. Artificial, sintered aluminum oxide cores were treated with organochlorosilanes to change the wettability from strongly water-wet. The plugs were saturated with gas and oil, then waterflooded. While the gas affected the oil saturation during the early stages of the waterflood, there was essentially no effect after 3 PV of water injection. In contrast, the residual oil in water-wet reservoir and sintered aluminum oxide cores was affected, declining as the trapped gas saturation increased.

Kyte *et al.* proposed that the wettability affected the results by controlling the fluid distributions in the core. In a water-wet core, the residual oil and gas are trapped in the centers of the pores, while the water occupies the rock surfaces. The trapped gas occupies a portion of the pore that would otherwise be occupied with residual oil; therefore, ROS is decreased by increasing the gas saturation. In contrast, the residual oil in an oil-wet system is located on the rock surfaces, while the gas and water are located in the centers of the pores. Because the residual oil and gas do not compete in oil-wet systems, ROS is not affected by trapped gas.

Effects of Core Cleaning and Handling

The experiments described attempted to vary wettability systematically. In this section, we will review some experiments that show how core cleaning and handling can drastically affect waterflood behavior by altering the wettability of core. Additional information on the effects of core cleaning and handling on relative permeability can be found in Ref. 5.

Keelan⁸⁹ examined the effects of contamination and core cleaning on waterflood recovery. Unsteady-state relative permeabilities were measured on an oil-wet weathered core with wettability-altering chemicals in the mud. A second set of relative permeabilities was measured after the core was cleaned and rendered water-wet by firing at 570°F [300°C] in an oxygen/CO₂ atmosphere to remove all adsorbed, wettability-altering compounds. Waterflood

TABLE 1—AVERAGE ROS IN PRESERVED AND CLEANED CORES⁹²

Reservoir	ROS (% PV)	
	Preserved-State	Cleaned
A	17.6	17.0
B	17.2	16.4
C	15.2	27.1

behavior was then calculated from the relative permeability curves, assuming an oil/water viscosity ratio of 4. A comparison of the two waterfloods is shown in Fig. 16. As expected, the waterflood in the water-wet core is more efficient. Note that the fractional flow of water is 95 % in the water-wet core after approximately 1.4 PV water is injected. In contrast, the oil-wet core requires roughly 2.2 PV of injected water to reach the same fractional flow, demonstrating the more rapid rise in WOR after breakthrough for water-wet systems.

Rühl *et al.*^{90,91} made two series of measurements on core from the Hohne reservoir that demonstrated the effects of core handling on waterflood behavior. In the first set of experiments, reservoir-condition waterfloods were compared in weathered cores vs. cores that were cleaned and extracted with a benzene/alcohol mixture. Both cores were flushed with brine, then driven to IWS with live crude. During the waterflood, the weathered cores acted more oil-wet, with earlier breakthrough and lower recoveries.

Rühl *et al.* also compared three sets of waterfloods on extracted core: (1) reservoir-condition waterflood with live crude and brine, (2) room-condition waterflood with dead crude oil, and (3) room-condition waterflood with a refined mineral oil. The viscosities of the dead crude and the refined mineral oil were reduced with gasoline to match the live crude. There was essentially no difference in behavior for waterfloods with live or dead crude. The waterfloods with the refined mineral oil were slightly more water-wet, with 2 to 3 % PV higher average recoveries at breakthrough and 5 % PV higher average recoveries after the injection of 3 PV of water. The experiments by Rühl *et al.* are valuable for demonstrating the effects of experimental conditions on waterflood behavior. However, note that none of the experiments were at the reservoir wettability. The cores were either weathered or extracted before the testing. Apparently, the extracted cores saturated with brine and crude were not aged before testing, so the wettability was probably not at equilibrium.

Luffel and Randall⁹² compared ROS's measured on preserved and cleaned cores from three reservoirs. The preserved cores were taken with a water-based mud, then sealed to prevent evaporation and wettability alteration. Preserved samples were flooded with brine and kerosene to IWS, then waterflooded to determine ROS. The samples were then cleaned, saturated with brine and kerosene, and waterflooded to determine ROS. The results are shown in Table 1. In two of the fields, there was essentially no difference in ROS for preserved vs. cleaned cores. In Reservoir C, however, the average ROS for the preserved cores was 15.2 %, vs. 27.1 % for the cleaned cores. For Reservoir C, Luffel and Randall state that the preserved core measurements are in better agreement with the ROS of 17.9 % calculated from the reservoir performance data.

Rathmell *et al.*⁴⁸ compared ROS's for native-state and cleaned plugs. Wettability was measured by the imbibition method on native-state plugs, while ROS's were determined on the native-state and cleaned plugs by waterflooding. The results are shown in Table 2. ROS was changed significantly in Reservoirs 2, 5, and 7. The ROS in Reservoir 2 increased from 15.8 to 33.2 % PV. Imbibition tests showed that the cleaned plugs from Reservoir 2 were strongly water-wet. An example of the change in waterflood behavior for Reservoir 2 before and after cleaning is shown in Fig. 12. The oil saturation in Reservoir 7 decreased about 15 % PV. Imbibition tests showed that Reservoir 7 was still oil-wet after cleaning; however, it is possible that the cleaning altered the location of some of the adsorbed, wettability-altering compounds. Unfortunately, the wettability of the other reservoirs after cleaning is not given. However, the results of Rathmell *et al.* indicate the strong effects of cleaning on ROS in some reservoirs.

TABLE 2—ROS IN RESERVOIR CORE PLUGS⁴⁸

Reservoir	Native-State Wettability	ROS (% PV)	
		Native-State	Cleaned
1	Weakly water-wet	27.3	31.6
2	Weakly water-wet	15.8	33.2
3	Weakly water-wet	44.8	47.0
4	Water-wet	37.5	35.2
5	Weakly water-wet	29.4	36.4
6	Weakly water-wet	17.0	18.3
7	Oil-wet*	35.1	20.5
8	Oil-wet, intermediate*	22.0	19.8

*Imbibed oil, no water.

**Imbibed both oil and water.

TABLE 3—ROS AT WOR = 100, FRACTIONALLY WETTED SANDPACKS⁹⁵

Oil-Wet Sand (%)	ROS (% PV)
0	28
25	35
50	40
75	45
100	48

Rathmell *et al.* also examined the effects on waterflood performance of aging outcrop sandstone cores with crude oil. The ROS of a 7-ft [2.1-m]-long Torpedo sandstone core was 43.5 % PV using brine and a refined mineral oil, with no oil production after water breakthrough. A water imbibition test on a second plug indicated that the core was water-wet, imbibing 40 % PV of water. The same core was aged with crude for 4 weeks at IWS, then waterflooded, causing ROS to decrease to 34.7 % PV. Again, no production after water breakthrough was observed. Imbibition tests on a plug indicated that the aged core was weakly water-wet, imbibing only 4 % PV of water.

Lorenz *et al.*²⁵ studied the effects of aging on waterflood behavior using Muddy J crude in outcrop Cottage Grove sandstone cores. Before aging, the system was water-wet, with essentially no production after breakthrough. After aging for several weeks, breakthrough occurred earlier, with a longer period of simultaneous oil and water production.

Fractional- and Mixed-Wet Systems

In the experiments in uniformly wetted porous media discussed previously, the wettability of the core was varied, while attempting to keep the wettability of the entire surface as uniform as possible. Many reservoir rocks have heterogeneous wettability, however, with variations in wetting preference on different surfaces. Additional wettability effects will occur when the system has nonuniform wettability (either fractional or mixed), where portions of the rock surface are water-wet, but the remainder are oil-wet.^{1,93,94} Salathiel⁹⁴ introduced the term "mixed" wettability for a special type of fractional wettability in which the oil-wet surfaces form continuous paths through the larger pores. The smaller pores remain water-wet, containing no oil. Note that the main distinction between mixed and fractional wettability is that the latter does not imply either specific locations for the oil-wet and water-wet surfaces or continuous oil-wet paths. In the fractionally wetted systems discussed, the individual water-wet and oil-wet surfaces have sizes on the order of a single pore.

Fractional Wettability. Fatt and Klikoff⁹⁵ measured the relative permeability ratio and the economical residual oil in fractionally wetted sandpacks formed by mixing treated and untreated sand grains together. The untreated sand grains were strongly water-wet, while the remaining sand grains were treated with Drifilm to render them oil-wet. Note that during mixing, some Drifilm may have been transferred to some of the water-wet sand grains, probably giving them a nonzero contact angle.⁹⁵ The absolute permeability of the

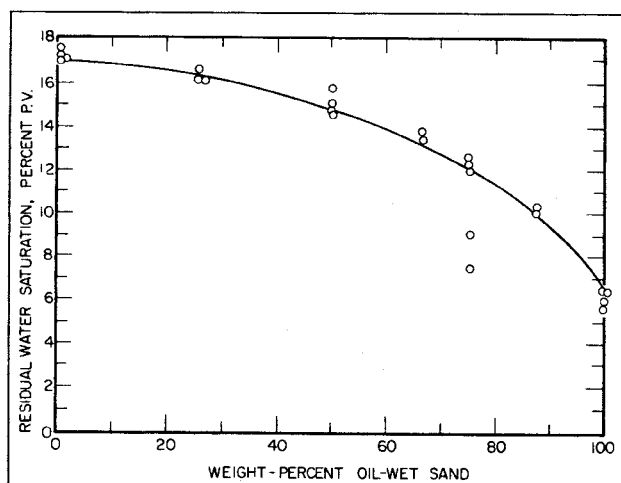


Fig. 17—Effect of fractional wettability on residual water saturation after the injection of 4 PV of oil. Taken from Iwankow.⁹⁹

sandpacks was roughly 3.2 darcies. The fractionally wetted sandpacks were saturated with water, driven to IWS with a 100-cp [100-mPa·s] refined mineral oil, then waterflooded. Table 3 gives the economical ROS measured at a WOR of 100. Clearly, ROS increases as the fraction of oil-wet surfaces increases, which is similar to the changes that occur as a uniformly wetted system becomes more oil-wet.

Talash and Crawford⁹⁶⁻⁹⁸ waterflooded a one-quarter five-spot model packed with different fractions of water-wet and organochlorosilane-treated, oil-wet sand grains. The fractional wettability, oil/water viscosity ratio, and initial water, oil, and gas saturations were all varied. For constant viscosity ratio and initial saturations, the oil recovery after 2 PV of water was injected decreased with increasing oil fractional wettability. This is consistent with the results of Fatt and Klikoff.⁹⁵

Iwankow⁹⁹ examined the effects of fractional wettability on residual water saturation using fractionally wetted sandpacks composed of cleaned and fired, water-wet sand grains and organochlorosilane-treated, oil-wet sand grains. The sandpacks were saturated with water, then injected with 4 PV's of a refined mineral oil. As shown in Fig. 17, the residual water saturation decreases as the fraction of oil-wet sand increases. This is consistent with the results of Fatt and Klikoff⁹⁵ and Talash and Crawford.⁹⁶⁻⁹⁸ All three experiments found that the practical residual saturation of a fluid increases as the percent of sand grains wet by that fluid increases. The practical ROS increases as the oil fractional wettability increases, while the practical residual water saturation increases as the water fractional wettability increases.

Singhal *et al.*¹⁰⁰ measured unsteady-state relative permeabilities and recoveries in fractionally wetted bead packs, where the fractional wettability was altered by changing the percentages of water-wet (glass) and oil-wet (teflon) beads. Distilled water and a series of refined organic liquids were used, which gave contact angles measured through the water that ranged from 40 to 77° [0.7 to 1.34 rad] for glass and 83 to 157° [1.45 to 2.74 rad] for the teflon. The glass was always the more strongly water-wet surface, while the teflon was always more oil-wetted for all of the fluid pairs used. The dry bead pack was first saturated by water, then flooded with an organic liquid to the residual water saturation. After cleaning, the dry bead pack was saturated with the organic liquid and waterflooded to the residual organic liquid saturation.

Generally, Singhal *et al.* found that the ultimate recovery of the displaced phase decreased slightly as the fractional surface area wetted to that phase increased. For example, the ultimate recovery of an organic liquid decreased as the percentage of oil-wet beads decreased. Unfortunately, the alterations in fractional wettability also changed the bead (and pore) size distribution, because the glass beads were roughly eight times larger in diameter than the teflon beads. The variations in pore geometry and specific surface area may also have affected the ultimate recovery.

In summary, fractionally wetted sandpacks, where the individual water-wet and oil-wet surfaces have sizes on the order of a single pore, behave similarly to uniformly wetted systems. The practical ROS increases as the fraction of oil-wet surface increases, and the waterflood behavior lies between the curves for 100% water-wet and 100% oil-wet sandpacks. Relative permeability and capillary pressure measurements as the fractional wettability is varied are also similar to measurements in uniformly wetted cores.^{4,5} In the next section, mixed-wettability cores with continuous oil-wet paths will be discussed. In mixed-wettability cores, the waterflood behavior is drastically different from uniformly wetted cores.

Mixed Wettability. In Salathiel's⁹⁴ mixed-wettability cores, because the large pores contain continuous oil-wet paths while the small ones are water-wet, the true ROS is much lower than the residual saturation obtained in uniformly wetted systems. In uniformly wetted core, the true ROS reaches a minimum when the core's wettability ranges from neutrally to weakly oil-wet, where the capillary forces are small. As the water-wetting tendency becomes stronger, ROS increases because there is a tendency to isolate oil in the larger pores. On the other hand, as the oil-wetting tendency becomes stronger, the true residual saturation also increases because capillary forces trap the oil in the smaller pores. Because these pores are oil-wet, there is no driving force for the water to displace the oil from them. However, most of the oil in the large pores is recovered. Because a mixed-wettability system combines the best aspects of water- and oil-wet systems, it reaches a low ROS. Compared with a water-wet system, trapping is reduced in the large, oil-wet pores. Compared with an oil-wet system, trapping is reduced because the small pores in a mixed-wettability system are water-filled.

Salathiel visualizes the generation of mixed wettability in the following manner. When oil initially invaded an originally water-wet reservoir, it displaced water from the larger pores, while the smaller pores remained water-filled because of capillary forces. A mixed-wettability condition occurred if the oil deposited a layer of oil-wet organic material only on those rock surfaces that were in direct contact with the oil but not on the brine-covered surfaces. Oil-wet deposits would not be formed in the small water-filled pores, allowing them to remain water-wet. In contrast to fractionally wetted sandpacks and uniformly wetted systems, the organized nature of the oil- and water-wet surfaces in mixed-wettability systems affects multiphase flow measurements, including capillary pressure,^{4,90,91,101,102} imbibition behavior,^{2,4,103-105} electrical properties,^{3,101} and relative permeability and waterflood behavior.^{5,13,94,101,103,106-108}

During a waterflood of a mixed-wet system, the small pores contain no oil to be trapped. In addition, the continuous oil-wet paths in the large pores allow oil to drain in films along the pore walls, causing a small but finite oil permeability to exist down to very low oil saturations. This, in turn, allows the waterflood to remove essentially all the oil initially present after the injection of many PV's of water. Richardson *et al.*¹⁰¹ waterflooded and oilflooded native-state East Texas Woodbine cores, which were later shown by Salathiel⁹⁴ to have mixed wettability. The initial waterfloods in the native-state core had very low ROS, with substantial oil produced at very high WOR's. After the injection of roughly 40 PV of water, ROS averaged about 12% PV for the nine native-state samples tested.^{94,101} Three of the cores had very low ROS's, on the order of 2% PV. After the initial waterflood, the cores were repeatedly oilflooded to IWS, then waterflooded. ROS gradually increased, probably because of either hysteresis effects or wettability alteration. The cores were then extracted. ROS after extraction was even greater, averaging 30% PV. Imbibition tests showed that the extracted core was more water-wet than the native-state core, because it imbibed water more rapidly.

After the experiments of Richardson *et al.*, Burkhardt *et al.*¹⁰³ made imbibition tests on preserved East Texas Woodbine plugs and found that the plugs would imbibe both water and oil, an indication of nonuniform wettability. Preserved cores were driven to ROS with brine, then allowed to imbibe kerosene. The cores were then driven to IWS with kerosene and allowed to imbibe brine. The aver-

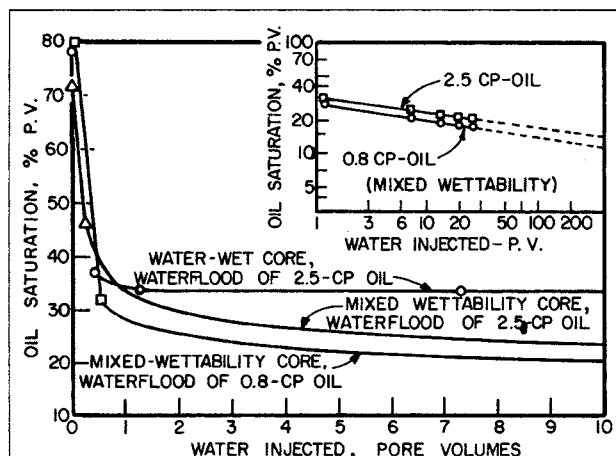


Fig. 18—Comparison of waterflood behavior for mixed-wet and water-wet cores (insert shows extension of mixed-wettability flooding data). Outcrop Boise sandstone core, brine, and either a 2.5-cp refined mineral oil or a 0.8-cp heptane/crude oil mixture were used. Mixed wettability was obtained by aging the core with brine and the heptane/crude oil mixture. Taken from Salathiel.⁹⁴

age amounts of oil and brine imbibition were 10.2 and 7.1% PV, respectively. The imbibition of both oil and brine is an indication that East Texas core has fractional or mixed wettability with both oil- and water-wet surfaces in the core.

Salathiel⁹⁴ observed waterflood behavior similar to the Woodbine core for a number of other fields at both reservoir and room conditions, postulating that the low ROS was caused by mixed wettability. He was able to generate mixed-wettability samples by aging outcrop Boise sandstone cores with brine and a mixture of dead crude and heptane was used because it would deposit a stable, strongly oil-wet film on glass or quartz surfaces in direct contact with the mixture, while adjacent areas of the surface in contact with brine remained water-wet. Initially, Salathiel tried dead crude, but found that oil-wet films that were generated after 3 days when only dead crude was used were much less stable and could be displaced by brine after a relatively brief contact. Note that if Salathiel had wanted to restore the wettability of an East Texas reservoir core, it would have been necessary to saturate the core with brine and crude, then age the core at reservoir conditions for a longer period of time. Because Salathiel was studying displacement mechanisms in mixed-wettability core, however, he did not need to reproduce reservoir wettability exactly. Cores were aged with brine and a crude/heptane mixture at room conditions because this was the most convenient method to generate mixed-wettability systems.

Fig. 18 compares waterfloods first in a strongly water-wet core, then in the same core with mixed wettability. First, the water-wet outcrop Boise sandstone core was saturated with brine, driven to IWS with a viscous refined mineral oil, oilflooded to replace the viscous mineral oil with a 2.5-cp [2.5-mPa·s] refined mineral oil, then waterflooded. Second, after cleaning, the core was saturated with brine, driven to IWS with a refined mineral oil, then oilflooded to replace the viscous oil with a 0.8-cp [0.8-mPa·s] mixture of heptane and East Texas crude. Next, the core was aged for several days to generate the mixed wettability, then waterflooded. Finally, the core was driven back to IWS, then waterflooded to displace the same 2.5-cp [2.5-mPa·s] refined mineral oil. Note that the three waterfloods had somewhat different initial oil saturations, with the initial saturation for the water-wet flood (about 79% PV) roughly halfway between the two mixed-wettability floods (85.2 and 72.1% PV for the 0.8- and 2.5-cp [0.8- and 2.5-mPa·s] oils). This increase in the IWS after the initial waterflood has been observed in other mixed-wettability systems and will be discussed in more detail.

As expected, the top curve of Fig. 18 shows that very little oil is produced after breakthrough when the core is strongly water-

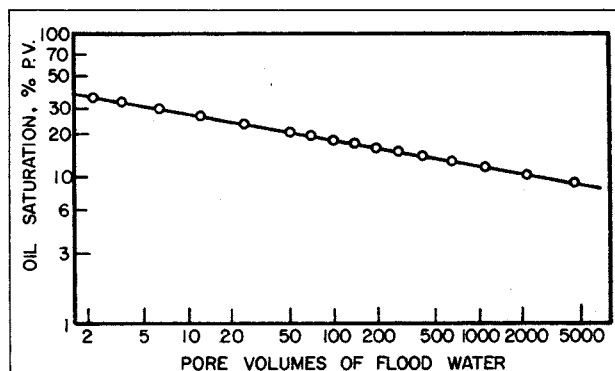


Fig. 19—Extended waterflood data on a native-state East Texas field core with mixed wettability. Taken from Salathiel.⁹⁴

wet. The final oil saturation is about 35%. In the mixed-wettability core, more oil is recovered after the injection of the same amount of water, and additional oil can be recovered by waterflooding until the economic saturation is reached. In the mixed-wettability core, the true ROS is surprisingly low, approaching 10% or less. The insert in Fig. 18 shows how the recovery keeps increasing and the oil saturation decreasing as many PV's of water are injected. Fig. 19 shows the recovery from a native-state Woodbine core that has mixed wettability. Again, increased recovery is obtained after the injection of many PV's of water so that the true ROS is very low, 9% or less. As in Fig. 18, the true ROS in Fig. 19 is not known because the core was still producing very small amounts of oil after 5,000 PV of water was injected.

Salathiel proposed that the very low ROS was obtained by oil draining through films on oil-wet surfaces in the large pores. Film drainage of oil on neutral- to oil-wet surfaces has been observed in micromodels. Mattax and Kyte³⁴ examined waterfloods in glass micromodels. Some of the models were saturated with brine, driven to IWS with crude, then aged for several hours. A visual examination of the fluid distribution after aging showed that some of the glass surfaces had become oil-wet, while the remainder were still water-wet. During waterfloods of these systems, some of the immobile oil behind the waterfront was still connected to oil ahead of the waterfront by thin filaments of oil on the pore walls, probably on the oil-wet surfaces. These thin filaments allowed a substantial portion of the bypassed oil to drain before they finally ruptured, trapping the remaining oil. Donaldson and Thomas²⁹ observed similar drainage through filaments during waterfloods in neutral- to oil-wet micromodels packed with sand.

Salathiel found that the generation of the mixed-wettability state was affected by the amount of water in the core during the aging process. Initially water-wet outcrop Boise sandstone cores were saturated with brine. The brine saturation was then reduced to the desired value, generally by flooding with a refined mineral oil, which was finally replaced with the mixture of heptane and East Texas crude. Very low initial water saturations were obtained by gasflooding the core, then evaporating some of the remaining water before flooding the core with a refined mineral oil. After flooding with the heptane/crude mixture, the core was aged for a period of 3 days to generate mixed wettability, then waterflooded. Fig. 20 shows the oil saturation during waterflooding plotted vs. water saturation during aging and film deposition. Each curve shows the oil saturation after the injection of the specified number of PV's of water. The top curve shows the oil saturation at breakthrough, while the bottom curve shows ROS after 20 PV of water injection. In comparison, an ROS of roughly 33% would be expected for strongly water-wet Boise sandstone cores. The minimum ROS (roughly 16 to 17%) occurred when the core contained approximately 13 to 20% interstitial water during aging. It appears that at lower aging water saturations, some of the small pores become oil-wet and trap oil, which increases ROS. On the other hand, ROS may increase at higher interstitial water saturations because portions of the larger pores remain water-wet, disturbing the continuity of the oil-wet paths.

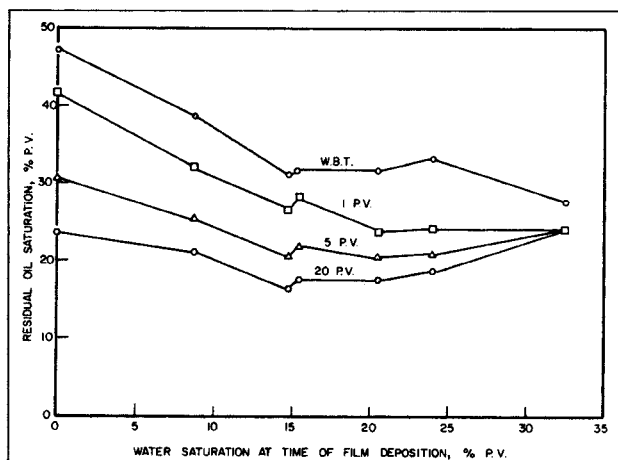


Fig. 20—How water saturation during deposition of oil-wet film affects ROS's left by waterfloods, 0.8-cp heptane/crude oil mixture and Boise sandstone. The top curve shows the oil saturation at water breakthrough, while the bottom curve shows the ROS after 20 PV of water injection. Taken from Salathiel.⁹⁴

After the initial waterflood, Salathiel found that the IWS was much higher than the interstitial water saturation at which the cores had been aged. Salathiel states that the IWS for mixed-wettability systems is frequently higher than the IWS obtained when the core is water-wet or when the mixed wettability is originally generated. To obtain the initial water saturation, it was necessary to clean and fire the cores to render them strongly water-wet, then repeat the procedure to generate mixed wettability. Richardson *et al.*¹⁰¹ also observed high IWS after the initial waterflood. They waterflooded their native-state Woodbine cores to a low ROS, then oilflooded them. IWS measured after the first oilflood was relatively high, with an average value of 40% PV. After the second oilflood, the average IWS decreased to 34% PV, possibly because of hysteresis or wettability alteration. After cleaning, IWS was only 20%. Richardson *et al.*,¹⁰¹ Rühl *et al.*,^{90,91} and Schmid¹⁰² found that the IWS measured during capillary pressure measurements was also higher for mixed-wet vs. water-wet cores. (For further discussion, see Ref. 4.)

At the beginning of an oilflood of a mixed-wet core, the oil will preferentially travel through the large, oil-wet pores. During this time, much of the water in the small, water-wet pores is held by capillary forces. Once the oil has displaced the water from the large pores, the water in the small pores is trapped and immovable. The IWS is lower for a strongly water-wet core because the water in the small pores remains connected through thin films on the pore surfaces and can still be displaced.

Because continuous, strongly oil-wet paths are needed for film drainage, the generation of mixed wettability is also affected by pore geometry and mineralogy. In addition to waterfloods in outcrop Boise sandstone cores, Salathiel aged Upper Austin sandstone, Lissie sandstone, Woodbine sandstone, and Upper Noodle limestone cores with brine and the heptane/East Texas crude mixture. Film drainage was obtained with only the Upper Austin and Woodbine samples. The Upper Noodle and Lissie cores had higher ROS's (20 and 26%, respectively) and no film drainage, indicating that mixed wettability was not obtained in these cores. Salathiel felt that the difference in behavior might be a result of mineralogy because the Upper Noodle is a limestone and the Lissie sandstone contained carbonate crystals.

Salathiel⁹⁴ also found that pore geometry was important in generating mixed wettability. He aged a glass bead pack with brine and the heptane/crude mixture and found that film drainage did not occur. This was explained by the difference in pore geometry between bead packs and consolidated cores. In bead packs, most of the irreducible water is held in the form of "pendular rings" at the point of contact between each pair of beads. These pendular rings prevent the deposition of continuous oil-wet paths between beads, preventing film drainage.

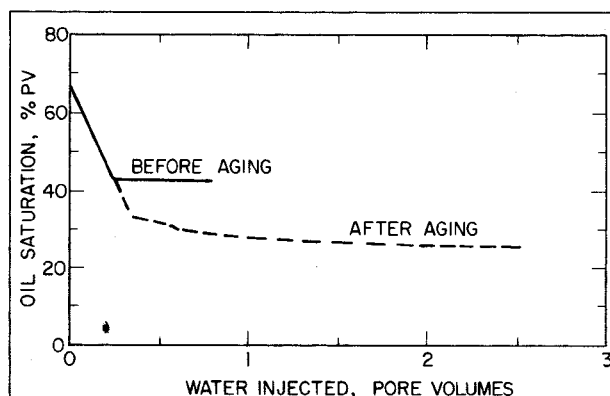


Fig. 21—Comparison of waterfloods in a Berea core before and after aging for 1 year with brine and Loudon crude at 160°F. Taken from Wang.¹⁰⁸

Patel *et al.*¹⁰⁷ obtained mixed-wet behavior in a Wason field (San Andres) core. The core was aged with interstitial water and dead crude oil for several days, flushed with a refined mineral oil to an initial oil saturation of 58.4%, then waterflooded. The oil saturation at the end of the waterflood was 20.8%, with small volumes of oil still being produced. The core was then extracted to alter its wettability, saturated with brine, oilflooded with a refined mineral oil to an initial oil saturation of 56.5%, and waterflooded. In contrast to the mixed-wet core, the waterflood was less efficient and no film drainage was observed. The final oil saturation was 33.9%, and oil production ceased before the waterflood was terminated.

Salathiel⁹⁴ and Patel *et al.*¹⁰⁷ were able to obtain mixed-wettability cores by aging water-wet cores with brine and crude. However, note that most cores restored in this manner will *not* have mixed wettability. Salathiel did not obtain mixed-wet behavior in cores from two reservoirs. In many of our experiments, we have found that restored-state cores are neutrally to mildly oil-wet, rather than mixed-wet (e.g., see Wendel *et al.*⁶²).

The wettability of a restored-state core is affected by a large number of factors, including the crude, the mineral surfaces, and the brine chemistry.¹ Mixed wettability will be generated when the crude deposits an oil-wet film only on surfaces that are in direct contact with the crude, but not in the small, water-filled pores. In some crude/brine/rock systems, however, the wettability can also be altered by the adsorption of surfactants from the crude. Over a long enough period of time, these compounds can diffuse through the interstitial water so that the wettability of the entire core, including the small, water-filled pores, becomes more oil-wet. Because the restored-state core may have mixed, fractional, or uniform wettability, the wettability must be determined by waterflooding, relative permeability, and wettability measurements.

Wang¹⁰⁸ found that native-state Loudon core appeared to be mixed wet because small amounts of oil were still being produced during waterfloods after more than 30 PV of water injection. To investigate this phenomenon, waterflooding experiments were then made with Berea core and Loudon crude. A clean, initially water-wet Berea core was saturated with brine, driven to IWS with Loudon crude, then waterflooded. After a number of other measurements, the core was driven to IWS with Loudon crude, aged at 160°F [71°C] for 1 year, flushed with fresh Loudon crude, then waterflooded. The results are shown in Fig. 21. Before aging, there was no significant oil production after breakthrough, with an ROS of 42.5%. The oil saturation at the end of the waterflood of the aged core was only 25.7%. Steady-state relative permeability measurements, where more water was injected, showed that ROS for the aged Berea was less than 17% PV. The water relative permeability at ROS was 35% of the absolute water permeability, while the water relative permeability of a similar unaged plug was only 3.4%. Wang found that the aged Berea plugs imbibed a smaller amount of water less rapidly compared with the plugs before aging. This indicates that the aged plugs were less water-wet. Unfortunately,

Wang did not measure oil imbibition, so it is not known whether portions of the aged core were oil-wet.

It is possible that Rathmell *et al.*⁴⁸ also waterflooded a mixed-wet core because the native-state waterflood in Fig. 12 is very similar to the waterflood of the aged Berea in Fig. 21. Unfortunately, it is not known whether film drainage would occur if the native-state core in Fig. 12 were injected with many PV's of water.

Morrow *et al.*¹⁰⁶ compared waterfloods in strongly water-wet Berea cores vs. floods when the cores were aged with brine and Moutray crude oil. The aged cores did not have mixed wettability, but may have had some type of heterogeneous wettability. The water-wet Berea cores were saturated with brine, driven to IWS with a refined mineral oil, and waterflooded. The aged cores were saturated with brine, driven to IWS (roughly 40%) with Moutray crude, aged for 24 hours, then waterflooded. Compared with the water-wet core, the aged cores behaved similarly to the results shown in Figs. 12 and 21. Breakthrough occurred later, with greater oil recovery. In contrast to the results shown in Figs. 12 and 21, however, oil recovery was essentially complete after 1.5 PV injection, indicating that no film drainage was occurring.

The aged cores imbibed less water than the water-wet Berea cores, indicating that the system was less water-wet. However, in contrast to the mixed-wettability systems, no oil was imbibed. The lack of oil imbibition and film drainage indicates that these cores did not have mixed wettability. However, there are some indications that the cores were nonuniformly wetted. First, the water relative permeability at ROS was lower after aging, even though ROS had decreased. For uniformly wetted systems, the water relative permeability at a given saturation generally increases as the system becomes less water-wet.⁵ In addition, contact-angle measurements showed that under certain conditions, Moutray crude would deposit a stable, oil-wet film on mineral surfaces. Morrow *et al.* proposed that aging with crude formed heterogeneous ("speckled") wetting. Unfortunately, the mechanism causing increased recovery with this wettability is not known.

In summary, mixed-wettability cores have continuous oil-wet paths through the larger pores, while the small pores are water-filled. When mixed-wettability cores are waterflooded, film drainage gives a very low ROS after the injection of many PV's of water. When reflooded with oil after the first waterflood, mixed-wettability cores have a high IWS. Mixed-wettability cores can imbibe both water and oil because the cores contain water-wet and oil-wet surfaces. Capillary pressure and electrical properties are also affected by mixed wettability. Mixed wettability can be generated in some cores by saturating the cores with brine and crude at IWS, then aging. In other cases, restored-state cores will not be mixed-wet, but will have fractional or uniform wettability.

Conclusions

1. Oil recovery during waterflooding is a function of wettability, pore geometry, fluid distribution, saturation, saturation history, and oil/water viscosity ratio. Wettability affects waterflooding by controlling the flow and spatial distribution of fluids in a porous medium.

2. During the waterflood of a strongly water-wet system at a moderate oil/water viscosity ratio, a large fraction of the OIP is recovered before breakthrough. After breakthrough, the water/oil production ratio increases rapidly, and little additional oil is produced after breakthrough. Because there is almost no oil production after breakthrough, the breakthrough, practical (economical), and ultimate ROS's are essentially equal and low.

3. During the waterflood of a strongly oil-wet system at a moderate oil/water viscosity ratio, water breakthrough occurs early and most of the oil is recovered after breakthrough. Waterfloods are less efficient in oil-wet systems than in water-wet systems because more water must be injected to recover the same amount of oil.

4. As the wettability of a system ranges from water-wet to oil-wet, the breakthrough and economical ROS's increase, so oil recovery decreases. The economical ROS is lower than the breakthrough saturation, and the difference between the two gradually increases, so that there is a longer period of simultaneous oil and water production. Small amounts of oil are produced for a long time after

breakthrough; therefore, the economical ROS depends on the number of PV's of water injected.

5. The breakthrough and economic recoveries are dependent on both wettability and the oil/water viscosity ratio. The decrease in oil mobility at high oil/water viscosity ratios causes a decrease in the oil recovery at breakthrough and an increase in the period of oil and water production for cores of any wettability. On the other hand, there will be a high oil recovery at breakthrough and little subsequent oil recovery even in a strongly oil-wet core when the oil/water viscosity ratio is very favorable. However, a waterflood in an oil-wet or intermediate-wet core is always less efficient than the waterflood in a water-wet core at the same viscosity ratio.

6. The ultimate ROS, the saturation after a large number of PV's of water are injected, is only weakly dependent on the wettability. It is slightly lower near neutral wettability (higher oil recovery), but changes much less than the breakthrough or economic oil saturations.

7. There is some disagreement on the effects of wettability as a core becomes very strongly water-wet compared with moderately water-wet systems. All three ROS's are essentially the same because there is little production after water breakthrough, with all the oil trapped in discontinuous globules. However, different experiments suggest that the ROS can decrease, remain the same, or increase, depending on such variables as heterogeneity, pore geometry, injection rate, and inlet and outlet end effects.

8. In fractionally wetted sandpacks, where the size of the individual water-wet and oil-wet surfaces is on the order of a single pore, waterflood behavior is similar to the behavior in uniformly wetted systems. The practical ROS increases as the fraction of oil-wetted surface increases, and the waterflood behavior lies between the curves for 100% water-wet and 100% oil-wet sandpacks.

9. In a mixed-wettability core, the larger, oil-filled pores are oil-wet and the smaller, water-filled pores are water-wet. The continuous oil-wet paths in the larger pores enable a mixed-wettability core to be waterflooded to a very low ROS by the injection of many PV's of water. Other multiphase flow properties, including capillary pressure, imbibition behavior, electrical properties, relative permeabilities, and IWS, are also affected.

10. The most accurate waterflooding measurements are made on native-state core, where the reservoir wettability is preserved. When such core is unavailable, the core should be cleaned and reservoir wettability restored. If a reservoir is oil-wet or intermediate wet, but a clean, water-wet core is used, both the breakthrough and economic recoveries will be overestimated. Recoveries will also be misestimated if the core has fractional or mixed wettability.

Nomenclature

f_w	= fractional flow of water
k_{ro}	= oil relative permeability
k_{rw}	= water relative permeability
L	= core length, in. [cm]
p_o	= oil pressure, psi [kPa]
p_w	= water pressure, psi [kPa]
P_c	= capillary pressure, psi [kPa]
S_w	= water saturation, %
u	= flow rate per unit cross-sectional area, in./min [cm/min]
W	= USBM wettability index
θ	= contact angle
θ_a	= apparent contact angle
μ_o	= oil viscosity, cp [mPa·s]
μ_w	= water viscosity, cp [mPa·s]

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Appendix—A Re-Examination of the Wettability in Warren and Calhoun's Experiments

Fig. 11, taken from Warren and Calhoun,⁸³ shows the breakthrough and ultimate recoveries during waterfloods in a sintered Pyrex glass core, where the wettability was varied with different concentrations of Drifilm. Apparent contact angles in the treated core were calculated from the displacement pressure, which is the capillary pressure at which water will first enter a plug entirely saturated with oil. On the basis of these measurements, Warren and Calhoun assumed that the wettability of their experiments varied from neutrally wet ($\cos \theta_a = 0$) to strongly oil-wet ($\cos \theta_a = 1$). With this interpretation, the results shown in Fig. 11 are in serious disagreement with the remainder of the literature cited in the text. First, the ultimate oil recovery occurs under very strongly oil-wet conditions ($\theta_a = 180^\circ$ [3.14 rad]). Second, the breakthrough and ultimate recoveries are very close, even when $\cos \theta_a = 0.4$, which is oil-wet. The other experiments cited in the text found large differences in the breakthrough and economical recoveries even at neutral wettability ($\theta = 90^\circ$ [1.57 rad], $\cos \theta = 0$). For example, see Figs. 3 through 5.

We feel that a better interpretation of Warren and Calhoun's data is that the wettability varies from mildly water-wet to mildly oil-wet. With this interpretation, the data from Warren and Calhoun's experiments agrees with the other literature cited in the text. There are two other reasons for believing that this interpretation is correct. First, most experiments that used Drifilm to vary wettability were able to obtain only mildly oil-wet surfaces. Second, apparent contact angles based on the displacement pressure are unreliable. In some cases, these measurements may indicate that a system is oil-wet when it is actually water-wet. We believe that this occurred in Warren and Calhoun's experiments.

The wettability of cores treated with organochlorosilanes depends on a large number of variables, such as the organochlorosilane used, the concentration, the treatment time, the time elapsed since the

surface was treated, and the pH of the brine.¹ While several experimenters have been able to obtain strongly oil-wet surfaces,^{57,109} many other researchers have reported that their treated surfaces were at most neutrally to very mildly oil-wet.^{48,110-112} Warren and Calhoun used an organochlorosilane treatment very similar to that used in the earlier work of Bethel and Calhoun.¹¹⁰ The maximum contact angle that Bethel and Calhoun were able to obtain with air and water was roughly 115° [2 rad] through the water, according to capillary rise measurements in treated glass capillary tubes. Most of the treated tubes were neutrally wet or slightly water-wet, with contact angles through the water of 90° [1.57 rad] or less. The maximum contact angle that Coley *et al.*¹¹¹ obtained with organochlorosilane treatments was 117° [2.04 rad]. The results of Bethel and Calhoun, and Coley *et al.* in the same laboratory, make it likely that the plugs used by Warren and Calhoun also ranged from mildly water-wet to mildly oil-wet.

Warren and Calhoun measured wettabilities ranging from neutrally wet to strongly oil-wet because they calculated apparent contact angles, θ_a , on the basis of the displacement capillary pressure.^{83,113} Unfortunately, this method has recently been shown to be unreliable and will sometimes indicate that a system is oil-wet when it is actually water-wet or vice versa.⁴ Morrow and Mungan,¹¹⁴ Morrow,¹¹⁵ and Morrow and McCaffery¹¹⁶ show that the apparent contact angle calculated from capillary pressure measurements has little relationship to the true contact angle, θ , measured on a flat plate. Positive displacement pressures can be measured even when the injected fluid is the wetting fluid. In this case, calculation of an apparent contact angle would indicate the wrong wetting fluid. Positive displacement pressures for both the wetting and nonwetting fluids, particularly when the core is initially 100% saturated with the other fluid, have been frequently reported in the literature.^{18,19,117-121} Morrow and McCaffery,¹¹⁶ McCaffery,¹¹⁹ and McCaffery and Bennion¹²² found that when the core was initially saturated with the nonwetting fluid, a positive displacement pressure was required to force the wetting fluid into the core for contact angles as low as 49° [0.86 rad]. This means displacement-pressure measurements would erroneously indicate this system to be oil-wet.

If some of Warren and Calhoun's plugs were weakly water-wet, the experiments cited show that it would be possible for them to measure a positive displacement pressure for water displacing oil from the core. Assuming a capillary tube model, the apparent contact angle calculated from the displacement pressure would erroneously indicate that the core was oil-wet. We feel that the work by Warren and Calhoun is very valuable, particularly because it contains the only experiments that clearly show the relationship between the breakthrough and ultimate residual saturations. Their measure of wettability, based on an archaic and inaccurate scale, however, should be corrected to range from mildly water-wet to mildly oil-wet. With this interpretation, their experiments agree with the other literature cited.

SI Metric Conversion Factors

cp	$\times 1.0^*$	E-03	= Pa·s
degrees	$\times 1.745\ 329$	E-02	= rad
dynes/cm	$\times 1.0^*$	E+00	= mN/m
$^\circ\text{F}$	$(^\circ\text{F} - 32)/1.8$		= $^\circ\text{C}$

*Conversion factor is exact.

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